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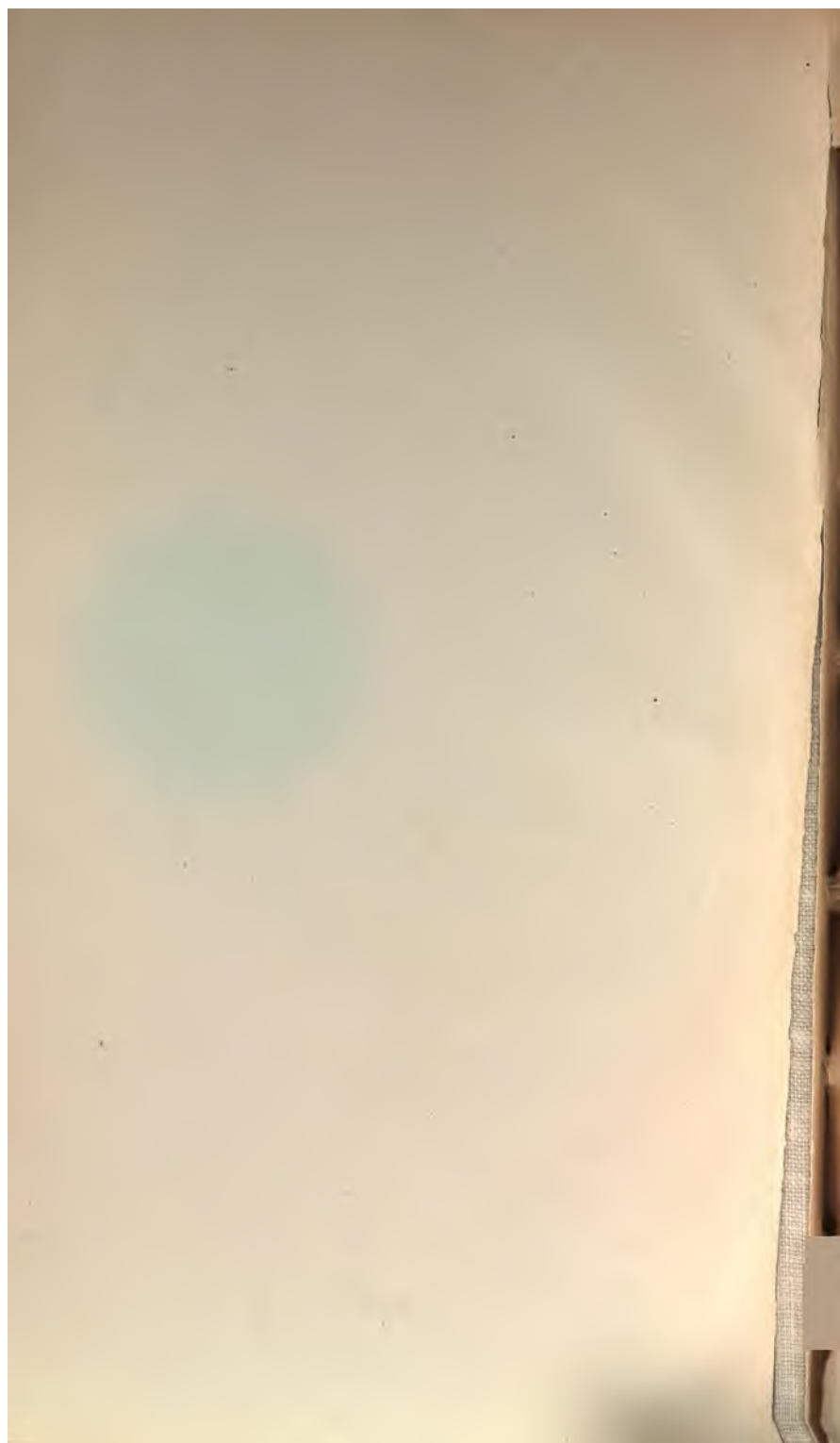


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LEAD AND ITS COMPOUNDS

LEAD

AND ITS COMPOUNDS

BY

THOMAS LAMBERT

TECHNICAL AND CONSULTING CHEMIST

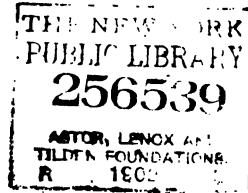
AUTHOR OF

"BONE PRODUCTS AND MANURES" ETC.

ILLUSTRATED BY FORTY PLANS AND DIAGRAMS

LONDON
SCOTT, GREENWOOD & CO.
19 LUDGATE HILL, E.C.
1902

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PREFACE.

IN the present volume the author has endeavoured to show the great strides made in the metallurgy of lead and zinc, and to incorporate in it the latest applications of electrical science, not only in cleansing the ores, but also in their after-treatment.

The work also contains a description of the pigments of both metals, their manufacture and properties; and to make this portion as comprehensive as possible, the drying oils and siccatives, and their relation to pigments, are dealt with. In addition to other information of importance to the colourist, the value of the work is enhanced by a chapter devoted to the assaying and analysis of lead and zinc ores, and the quantitative testing of paints and oils.

The book is divided into seventeen chapters, and is illustrated with forty drawings, specially made by Mr. Levi Lambert, to whom great credit is due.

In conclusion, the author hopes the work will be studied with advantage by those engaged in the above branches of industry.

THOMAS LAMBERT.

July 1902.

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several passages. The treasures of Solomon included not only gold and silver, but also lead. In Proverbs, mention is made of a silver dross, which was probably the oxidised lead left in the winning of silver from the galena ore, and used as a glaze for earthenware. In describing "the riches and abundance" of Tyrus, Ezekiel makes reference to lead, along with other metals, traded at the fairs of Tarshish. The enterprising and industrious Phœnicians largely derived their opulence from the trading in lead and silver. According to tradition, they sailed to the Iberian peninsula, discovered the Bay of Cadiz, and bartered oil for the lead and silver of the natives, carrying their treasures back to Asia to adorn the temples of Solomon. At a later age, Rome, then in the zenith of its power, cast covetous eyes on the mineral wealth of the Peninsula, and, disputing with Carthage for its possession, succeeded in 45 B.C. in conquering the country. Then commenced that extensive system of mining and smelting, which for grandeur of conception and mechanical genius have astonished metallurgists of the present age. During the occupancy of the Romans, extending to four centuries, some of the mines were carried to a depth fully equal to any presently working. At Caberzo-Rejado, in the province of Murcia, the remains of ancient mining have been found at a depth of 1000 feet from the surface. The vast extent of the operations may be gathered from the existence of our 30 million tons of metallic slag, found around Huelva, and which would represent about $1\frac{1}{4}$ million tons of metal smelted from the ores, mined by the Romans. Pliny says that 20,000 slaves were employed in these mines, and that at times the Roman army took part in their development. Among the many curiosities brought to light relating to Roman mining in Spain, may be mentioned a copper slab discovered in one of the mines at Huelva, in July 1772, and containing an inscription showing that the mine was in

charge of Procurator Pudente, during the reign of the Emperor Nerva.

British lead-mining may be said to have had its origin in that pre-Roman period, when the Phœnicians visited Cornwall in quest for tin. Our knowledge of their operations is, however, very obscure and untrustworthy. It was not until several centuries had elapsed, and the country came under the dominion of the Romans, who landed on our shores under the command of Julius Caesar in 55 B.C., that we find any tangible evidence of the development of lead-mining. During the 400 years of their occupancy, they industriously worked the counties of Cumberland, Westmoreland, York, Derby, Somerset, Devon, and Cornwall for their mineral wealth. With the decline and fall of the Roman Empire, and the consequent withdrawal of her military power from this country, lead-mining fell into decay, continuing in this condition for several centuries.

According to Hunt, the rich silver-lead veins of Devonshire, notably at the Coombe Martin and Beer Alston mines, were largely worked in the reigns of Edward I. and Edward II., chiefly for the silver they contained; and the same authority states that Henry VII. and Queen Elizabeth fostered the industry by importing German miners to work the lead mines in different parts of the country. In the eighteenth century the production of lead and silver was very low, and the last century was well advanced before the industry assumed a

	1861-62.	1890-91.
England and Isle of Man	226 (no return for Derbyshire)	411
Wales	147	2
Scotland	7	4
Ireland	7	3

national importance by the opening up of new mines, and the introduction of modern mining machinery.

The table on the preceding page gives the returns under the Metalliferous Mines Regulation Acts of the working lead mines for the years 1861-62 and 1890-91.

In 1890-91 England is credited with 293 mines, located in the limestone formation of Derbyshire. Many of the mines, however, are only small workings, each yielding but a few tons of galena ore in the year.

Ores of Lead.—The following ores, in which lead forms one of the principal constituents, are known to mineralogists:—

Aciculite	$\left. \begin{matrix} \text{Pb}_2 \\ \text{Cu}_2 \end{matrix} \right\} \text{S}_3 \cdot \text{Bi}_2\text{S}_3$.
Altaite	Telluride of lead— PbTe .
Anglesite	Sulphate of lead— PbSO_4 .
Aræoxene	Zinckeferous vanadate of lead.
Arsenomelane	$2\text{PbS} \cdot \text{As}_2\text{O}_3$.
Binnite	A mixture of the minerals—arsenomelane and scleroclase.
Bleinierite	Antimoniate of lead— $\text{Pb}_3\text{Sb}_2\text{O}_8 \cdot 4\text{H}_2\text{O}$.
Boulangerite	Antimonial sulphide of lead— $3\text{PbS} \cdot \text{Sb}_2\text{S}_3$.
Bournonite	Sulphides of copper, antimony, and lead— $(2\text{PbS} \cdot \text{Cu}_2\text{S})\text{Sb}_2\text{S}_3$.
Brogniardite	Sulphides of lead, antimony, and silver— $\text{Pb} \cdot \text{Ag}_2\text{S}_2 \cdot \text{Sb}_2\text{S}_3$.
Caledonite	Cupreous sulphato-carbonate of lead— $(\text{Pb} ; \text{Cu})\text{CO}_3 \cdot \text{PbSO}_4$.
Cerasin	Chloro-carbonate of lead— $\text{PbCl}_2 \cdot \text{PbCO}_3$.
Cerussite	Native white lead ore— PbCO_3 .
Chileite	Vanadate of lead and copper— $(\text{Pb} ; \text{Cu})_3(\text{VO}_4)_2 \cdot 3(\text{Pb} ; \text{Cu})\text{O}$.
Chiviatite	$2\text{PbS} \cdot 3\text{Bi}_2\text{S}_3$.
Clausthalite	Selenide of lead— PbSe .
Cotunnite	Native chloride of lead— PbCl_2 .
Crocoisite	Yellow chromate of lead— PbCrO_4 .
Cuproplumbite	Sulphides of lead and copper— $2\text{PbS} \cdot \text{CuS}$.
Dechenite	Vanadate of lead— PbV_2O_6 .
Descloizite	$2\text{PbO} \cdot \text{V}_2\text{O}_5$ or $\text{Pb}_2\text{V}_2\text{O}_7$.

Embrothite . . .	Antimonial sulphide of lead— $3\text{PbS} \cdot \text{Sb}_2\text{S}_3$.
Eusynchite . . .	Vanadate of lead— PbV_2O_6 .
Freislebenite . . .	Antimonial sulphides of lead and silver— $\text{Pb}_3\text{Ag}_4\text{S}_5 \cdot 2\text{Sb}_2\text{S}_3$.
Galena . . .	Sulphide of lead— PbS .
Geocronite . . .	Arseniferous schulzite.
Heteromorphite . . .	Antimonial sulphide of lead— $2\text{PbS} \cdot \text{Sb}_2\text{S}_3$.
Hydroaluminous lead .	Hydrated aluminate of lead— $\text{PbAl}_4\text{O}_7 \cdot 6\text{H}_2\text{O}$.
Jamesonite . . .	Antimonial sulphide of lead.
Kilbrickenite . . .	$6\text{PbS} \cdot \text{Sb}_2\text{S}_3$.
Kobellite . . .	Antimonial sulphides of lead and bismuth— $\left(\begin{array}{c} \text{Pb}_3 \\ 2\text{Sb} \cdot 3\text{Bi} \\ \hline 5 \quad 5 \end{array} \right)_2 \text{S}_6$.
Lanarkite . . .	Sulphato-carbonate of lead — $\text{PbCO}_3 \cdot \text{PbSO}_4$.
Lead glance . . .	Syn. with galena.
Lead . . .	Native.
Lead ochre . . .	Native protoxide of lead— PbO .
Leadhillite . . .	Sulphato-tricarbonate of lead— $3\text{PbCO}_3 \cdot \text{PbSO}_4$.
Lehrbachite . . .	Selenide of lead and mercury— $(\text{Pb} \cdot \text{Hg})\text{Se}$.
Linarite . . .	Cupreous sulphate of lead— $(\text{CuH}_2\text{O}_2 \cdot \text{PbSO}_4)$.
Matlockite . . .	Oxychloride of lead— $\text{Pb}_3\text{Cl}_2\text{O}$.
Melanochroite . . .	Chromate of lead— $3\text{PbO} \cdot 2\text{CrO}_3$.
Mendipite . . .	$\text{Pb}_3\text{Cl}_2\text{O}_2$.
Meneghinite . . .	Antimonial sulphide of lead— $4\text{PbS} \cdot \text{Sb}_2\text{S}_3$.
Mimetesite . . .	$\text{PbCl}_2 \cdot 3\text{Pb}_3\text{As}_2\text{O}_8$.
Minium . . .	Red oxide of lead— Pb_3O_4 .
Nagyagite . . .	Telluride and selenide of lead and gold— $(\text{Pb} ; \text{Au}_2)(\text{Te} ; \text{Se})$.
Needle ore . . .	Syn. with aciculite.
Patrinite . . .	" "
Phenicite . . .	Chromate of lead— PbCrO_4 .
Phosgenite . . .	Chloro-carbonate of lead.
Plattnerite . . .	Peroxide of lead— PbO_2 .
Plumboresinite . . .	Syn. with hydroaluminous lead.
Plumbostib . . .	Syn. with boulangerite.

Polysphærite . . .	Chlorophosphate of lead with calcium chloride— $3\text{Pb}_3\text{P}_2\text{O}_8 + \text{PbCl}_2 + \text{CaCl}_2$.
Schulzite . . .	Antimonial sulphide of lead— $5\text{PbS} \cdot \text{Sb}_2\text{S}_3$.
Selenate of lead . . .	PbSeO_4 .
Stolzite . . .	Tungstate of lead— PbWO_4 .
Sulzannite . . .	Rhombohedral sulphato-tricarbonate of lead— $\text{PbSO}_4 \cdot 3\text{PbCO}_3$.
Vanadinite . . .	$3\text{Pb}_3\text{V}_2\text{O}_8 \cdot \text{PbCl}_2$.
Vanquelinite . . .	Chromates of lead and copper— $\left. \begin{array}{l} 3\text{CuO} \\ 6\text{PbO} \end{array} \right\} 4\text{CrO}_3$
Wölchite . . .	Syn. with bournonite.
Wulfenite . . .	Molybdate of lead.
Zinckenite . . .	Antimonial sulphide of lead— $\left. \begin{array}{l} \text{PbS} \cdot \text{Sb}_2\text{S}_3 = \text{Pb} \\ \text{Sb}_2 \end{array} \right\} \text{S}_4$

Excepting galena or sulphide of lead, cerusite or carbonate of lead, anglesite or sulphate of lead, and, to some extent, mimetesite or the arsenate of lead, these ores, owing to their sparse occurrence, are only interesting to the mineralogist; even if they could be profitably mined, many would be unsuitable for metallurgical purposes.

Galena is the most important and abundant of the ores of lead, and it is the chief smelting mineral, not only for lead, but silver also, which is associated with it in the form of silver sulphide. Cerusite and anglesite are used also for lead extraction, but, from their limited distribution, are mined in far less quantities. Mimetesite finds a partial use in flint-glass making.

Galena.—The ore when pure has a composition of—

Lead	86.65
Sulphur	13.35
	<hr/>
	100.00

When mined, however, it is generally impregnated with small quantities of the sulphides of silver, antimony, and

zinc, and interspersed with particles of fluor-spar, quartz, calc-spar, or dolomite, according to the geological formation carrying the veins.

The following analyses of cleansed ore, by the author, express the composition of galena :—

	Spain.	England.		Scotland.
		Stonecroft.	Roman Gravels.	Lead Hills.
Lead	83·79	85·71	85·22	86·29
Silver	0·01	0·03	0·018	0·07
Antimony	0·12
Zinc	0·14	0·26	...
Iron	0·28	0·05	0·11	...
Sulphur	15·80	14·07	14·39	13·64
	100·00	100·00	99·998	100·00

Galena has a metallic lustre, and is of a lead-grey colour. The specific gravity ranges from 7·3 to 7·6, and the hardness from 2·5 to 2·7. On charcoal, before the blowpipe, the ore fuses, and is then reduced to the metallic state with evolution of sulphurous acid fumes, the globule of lead formed containing the whole of the silver, which is separated by cupellation.

When partly roasted in contact with air, galena is oxidised to sulphate and monoxide of lead, and these compounds again reacting on further portions of the sulphide, reduction to the metal takes place with liberation of sulphurous acid gas. The ore is very widely distributed, being found in more or less quantities, in nearly every country of the globe. Nor is it confined to one geological period. In England the rich lodes or veins of Derbyshire, Yorkshire, Cumberland, Westmoreland, and Durham, exist in the mountain limestone of the Carboniferous age; the lead "Killas" of Devon and Cornwall, in the Devonian; while the clayslates and gritstones of the Silurian

formation, mainly claim the deposits of the Welsh lead-bearing counties. To this epoch also, belong the lodes or veins of the Lead Hills and Wanlockhead in Scotland, and Laxey, Isle of Man. At Glenmalure and Luganure in Co. Wicklow, and Newtownards, Co. Down, Ireland, galena is chiefly mined from the granite rocks. The German deposits of galena in Silesia, Hanover, Westphalia, and the Rhineland districts, and also those in the Hartz mountains, are obtained from the Devonian strata. The Triassic, the Granite, and the Silurian ages, claim the Spanish galena deposits, as they exist in the southern provinces of the Peninsula. In the United States the extensive lead regions bordering the Mississippi, belong to the Silurian formation; and many of the Australian silver-lead lodes, are located in beds of fine-grained sandstones, shales, and mudstones.

Cerussite or Carbonate of Lead.—Cerussite is a natural derivative of galena, produced by decomposition and oxidation, and in a pure state has a composition of—

Oxide of lead	83.514
Carbonic acid	16.486
	<hr/>
	100.000

When pure, the ore exists in the form of colourless and transparent crystals. Generally, however, it occurs in fibrous, compact, and earthy masses of a white or greyish colour, and found mixed with galena in beds of mountain limestone. Sometimes it exists, contaminated with native copper salts, which give a blue tinge to the ore. The crystalline form belongs to the rhombic system. Cerussite has a hardness varying from 3 to 3.5, and an adamantine, inclining to vitreous, lustre. The specific gravity is 6.46. When treated with nitric acid it dissolves with considerable effervescence, liberating carbonic acid gas and forming a soluble nitrate of lead. On charcoal, before the blowpipe, it is quickly reduced

to the metallic state. Although the most abundant of the oxy-compounds of lead, but little is used for smelting purposes in this country, owing to its scarcity. In the Rhine-land districts of Aix-la-Chapelle and Cologne, and at Salander in Spain, considerable quantities are mined and smelted for the metal.

Anglesite or Sulphate of Lead.—This ore is an oxidised galena. In external characteristics it is similar to cerusite. When pure it has a composition of—

Oxide of lead	73·59
Sulphuric anhydride (SO ₃)	26·41
	<hr/>
	100·00

The crystals of anglesite have a rectangular octahedron form, with a hardness of 3 and a specific gravity of 6·25. With hydrochloric or nitric acid, no action takes place, and, on the addition of sulphuretted hydrogen, sulphide of lead is but slowly formed. Anglesite is found in the upper portion of many galena veins in Devon and Cornwall, in England; Lead Hills and Wanlockhead, in Scotland; Co. Wicklow, Ireland; and in America, France, and Germany. It is smelted along with galena ores.

Mimetesite or Arsenate of Lead.—The ore is rarely found pure. It is chiefly associated with phosphate and chloride of lead, and has a colour varying from brown to red. At times chromate of lead forms one of its constituents, giving an orange-yellow tinge to the mineral.

The following analysis represents its composition :—

Arsenate of lead	86·16
Phosphate of lead	6·45
Chloride of lead	7·39
	<hr/>
	100·00

Mimetesite has a hardness of 3·5 and a specific gravity

ranging from 5.17 to 5.49, and, when found in the crystalline state, the crystals take the form of a prism with six faces. On charcoal, before the blowpipe, it is easily reduced to metallic lead, with evolution of arsenical vapours. The mineral is generally found near the outcrop of galena veins in Cornwall, Devon, and Cumberland, in Saxony and in France.

Deposition of Lead Ore in Veins.—Notwithstanding the great strides geology has made within the last fifty years, it cannot be urged that this advancement has brought within the range of practical solution, our knowledge of the laws regulating the deposition of mineral matter in veins. That knowledge still remains purely speculative, and, in a sense, we are as much in the dark, as was Agricola, in ages past. By all writers, the phenomena of the formation of metallic veins have been ascribed either to the agency of fire or of water.

The Plutonic school, consisting of Stahl, Playfair, Hutton, and others, considered all veins to have been formed by subterranean heat, while Professor Cotta, another disciple of the same school, assumes that "the metals originated in the depths of the earth, and that, under the influence of heat, they have been sublimed, to be deposited in the colder cracks near the surface."

Dr. Hutton, in his work on the *Theory of the Earth*, forcibly advocates the Plutonic theory. He says: "Look into the sources of our mineral treasures. Ask the miner from whence has come the metal in his veins. Not above, nor from the strata which the vein traverses; these do not contain one atom of the minerals now considered. There is but one place from whence those minerals may have come—this is the bowels of the earth, the place of power and expansion; the place from whence has proceeded that intense heat by which loose materials have been consolidated into rocks, as

well as that enormous force by which the regular strata have been broken up and displaced."

Directly opposed to this, is the theory advocated by many modern writers on the subject, that mineral deposits in veins were formed solely by the agency of water, the water being supposed by some authorities to be of an atmospheric, and by others, of an oceanic character.

Wallace, in supporting the view that the water employed is atmospheric, and not oceanic, assumes that the original rocks contained mineral matter, and that the fissures or cracks were brought about by the upheaval of the earth's crust. The atmospheric water charged with oxygen and carbonic acid, on falling, penetrated the rocks, dissolving out the mineral constituents, and thence, after saturation, flowing into the crevices and depositing the mineral matter held in solution.

The balance of opinion seems to run more in favour of a hydrous than a Plutonic solution of the intricate problem; and further, that the former agency derived its existence from oceanic currents, as advocated by Werner, and not from an atmospheric source, as suggested by Wallace. This view is supported by the investigations of Moore, who discovered in eight samples of Allenhead galena ore, distinct signs of a fossiliferous existence. In the Weardale district also, the ore was found to be fossiliferous. This fossilised existence of what was once life that thronged the sea in the prehistoric ages, fully supports the theory of the marine origin of lead deposits.

CHAPTER II.

GEOGRAPHICAL DISTRIBUTION OF THE LEAD INDUSTRY.

IN nearly every country lead-smelting is carried on as a more or less important industry, owing to the universal deposits of galena and other lead ores. From the consular reports furnished to our own Government and that of the United States (the author is indebted to these sources for the matter contained in the following pages) it is noticed that the world's production of lead ore was in 1899, 775,000 tons, being an increase during the last decade of 235,000 tons. Of this grand aggregate, Spain contributed 308,660 tons, and this yield was increased to 350,000 tons for 1900. The Peninsula may be considered as the leading producer, and it owes this advantage to an abundance of mineral wealth, with low cost of labour and transport. The ore mined is, in part, argentiferous and non-argentiferous, the proportions for 1899 being 184,906 tons and 123,754 tons respectively. The mines of Jaen contributed the whole of the latter, and, of the former, the province of Murcia yielded 133,582 tons.

The lead-mining districts are in Jaen, Almeria, Cordova, Oviedo, Murcia, Badajoz, Ciudad Real, and Tarragona. The quality of the ore varies, some rich silver-galena lodes running to 80 per cent. lead, with 200 to 300 oz. of silver per ton. The low-grade ores of Caberzo-Rejado, are found mixed with pyrites, blende, quartz, and slate, and are designated as mantel or vein ores; they average 50 to 55 per cent.

lead. By far the largest proportion of ore raised is smelted in the country, and exported in the form of "pig" or sheet lead, the yield of the metal for 1899 being 162,613 tons, and valued at £2,469,000. The ore exported for that year was 9798 tons, and this quantity had decreased to 4632 tons for 1900, thus showing that the Spaniards are realising the immense importance of smelting their mineral wealth, instead of exporting it in the raw state.

The metallurgical operations are carried on in the Tuyere or Piltz furnaces, the fuel used being coke, the galena ores being previously calcined in a reverberatory furnace. The average percentage of metal got by smelting is 94 per cent. ; a loss of 5 per cent. through volatilisation and 1 per cent. left in the slags makes a total of 6 per cent. of unrecovered lead.

Receiving the largest proportion of her material ("pig" lead) from Spain, this country is unable to compete in Spanish markets, and this fact was so apparent a few years ago to one of the leading lead manufacturers that they erected works for the production of sheets, tubes, and shot, near their mines at Linares ; and, instead of sending their "pig" lead to England, as formerly, for treatment, they now export it in its manufactured state not only to England, but also to France and other countries.

United States.—As a lead-producing country, the United States ranks next to Spain. In 1899 the ore mined was 220,000 tons, and this yield had risen in 1900 to 233,000 tons, being an increase of 13,000 tons. The great silver-lead deposits in the valleys of the Mississippi and Missouri, and in Montana and Colorado, are being rapidly opened out, and as more outlets are found for the metal, accompanied with more remunerative prices, the time will not be far distant when the Republic will control the lead markets of the world.

Germany.—The yield of lead ore in 1899 was 129,200 tons, and, in 1900, 145,000 tons, being an increase of 16,000 tons. The deposits—mainly galena—are widely distributed, being mined in Silesia, Hanover, Westphalia, Hesse-Nassau, and the Rhineland districts of Coblenz, Cologne, Aix-la-Chapelle, and Dusseldorf. The ores vary considerably, ranging from 20 to 80 per cent. lead. The low-grade ores, which form the bulk of the deposits, are brought, for smelting purposes, to a percentage of 50 to 55 by a dressing and washing process.

The mines at Letmake, near Barmen, are worked comparatively near the surface, having a depth only from 130 to 180 feet. The ore is raised like coal, and the average percentage after washing is 40.

Near Dusseldorf, in the Rhine valley, the mines of Selbeck and Lintorf reach a depth of 900 feet, and the average, in the washed ore, is 50 per cent. lead. On smelting these ores, 90 to 92 per cent. of the metal is obtained, there being a loss of 8 to 10 per cent. through volatilisation and in the slags.

Around Frankfort-on-the-Main, some of the mines are carried to a depth of 1500 feet, the ore raised being of low-grade quality, yielding, after washing, 45 per cent. of lead.

In the Hartz mountains, embracing the duchy of Brunswick and the province of Hanover, the lead industry is a very important one, and dates from the Middle Ages. The deepest shaft is the Samson (2560 feet), yielding silver-lead, zinc, and copper ores. The silver averages .1 per cent., and the yield of lead by smelting, is 94 per cent. By a mechanical process, the zinc ores are separated and sold; when, however, small proportions are only present, the ores are not so treated, but smelted direct. The general method of treating the ores is first to calcine, which partly eliminates

the sulphur, and then reduce by smelting in the blast furnace.

Germany imports a considerable quantity of "pig" lead from Spain, and exports a good tonnage of manufactured products—sheets, pipes, and shot, litharge, white and red leads.

Austro-Hungary.—Lead ores are obtained in the provinces of Bohemia, Moravia, Silesia, Styria, Carinthia, Tyrol, Carniola, and Galicia. In all cases, the ores are extracted through shafts, the deepest being at Příbram, in Bohemia (1150 feet). Austro-Hungary mines large quantities, but the quality is poor, being mixed with earthy and silicious matter, and the ores require dressing and washing before undergoing smelting. The greater portion raised is smelted and desilverized within the country, and for this purpose the Government carry on extensive smelting works at Příbram. The other provinces also smelt, but the works are of less dimensions; those at Littai, in the province of Carniola, employ thirty-five men and smelt about 3500 tons of prepared ore each year. After preparatory treatment, the ores have an average of 60 per cent. lead and .1 per cent. of silver. The processes employed for obtaining the metal consist first in roasting the ore in a reverberatory furnace, which partly converts the sulphide into sulphate of lead, and then smelting in a blast furnace with wood, charcoal, brown coal, and coke. The blast furnace is chiefly used for treating rich argentiferous ores. On a charge of 10 tons, the fuel employed amounts to 7 tons brown coal, $2\frac{3}{4}$ tons coke, 354 cubic feet of charcoal, and $11\frac{1}{2}$ cubic feet of wood.

Austro-Hungary sells its surplus ores, and is also a buyer of "pig" lead, which is used in conjunction with its own production, for conversion into pipes, sheets, plates, litharge, sugar of lead, and white and red leads.

France.—The lead districts of France lie in the middle,

the north, and the west, and the production is about 22,000 tons annually. In the mines near Pontigbaud, the ores raised are of poor quality, but, by subsequent dressing and washing, they are brought up to 44 to 45 per cent. lead. The yield of silver is, however, considerable, averaging nearly 3 lb. per ton of ore. The Pontigbaud mines yield about 600 lb. silver per month.

In the south, lead and zinc ores are mined at Bormettes, the galena being of low grade and requiring treatment to bring it up to a smelting strength. Around Limoges, a low-grade galena is also raised, and, after washing, is smelted in a reverberatory furnace to extract the metal. The working loss is low, being only 3 to 4 per cent.

France is unable to supply her own requirements, consequently she imports large quantities of "pig" lead, and also sheets, pipes, and shot.

Great Britain and Ireland.—The lead-mining industry in the British Islands cannot be considered as a progressive one. This state arises from the decreased output, consequent on the exhaustion of some of the mines and the unprofitable results in working others, in face of the large imports of the foreign metal. In 1861, 12 counties in England, 9 in Wales, 6 in Scotland, and 5 in Ireland, were profitably engaged in raising lead ore. At the close of 1898 the English and Welsh returns embraced only Derbyshire, Flintshire, and the Isle of Man, while the mines of Scotland and Ireland were entirely closed. There is hope that with the advent of more remunerative prices, many of the mines in Durham, Northumberland, Westmoreland, and York, and in the Welsh counties of Cardigan, Denbigh, and Carnarvon, will again have a share of prosperity.

From the reports under the Metalliferous Mines Regula-

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tion Acts, the quantities of ore raised, with the smelting returns, are given as follows :—

ORE RAISED IN TONS.

	1861.	1889.	1898.	1899.
England and Wales	...	44,402	32,985	41,500
Scotland . . .	75,000	4,063	Mines closed.	Mines closed.
Ireland	218	„ „	„ „

YIELDS OF SILVER AND LEAD.

	1861.		1889.		1898.		1899.	
	Oz.	Tons.	Oz.	Tons.	Oz.	Tons.	Oz.	Tons.
England and Wales	280,374	32,281	211,403	25,728	260,000	32,370
Scotland . . .	473,538	58,500	24,493	3,163	None	...	None	...
Ireland	832	160	None	...	None	...

As mentioned, lead-mining is presently confined to the counties of Derby, Flint, and the Isle of Man. Devon and Cornwall formerly raised a large proportion of the country's output of ore ; consequent, however, on a number of the mines becoming exhausted, and, in others, the lodes or veins running below the water level, causing frequent inroads of water to the workings, and which necessitated their abandonment, the industry has fallen into decay. In 1861 the two counties were working fifty-five mines ; at the present time not a ton of ore is raised.

In Montgomery, Carnarvon, Denbigh, and other lead-bearing Welsh counties, the lodes have only been worked down to certain depths, owing to their being "cut" by non-bearing measures, 220 to 230 yards below the surface, rendering further mining operations unprofitable.

The North Riding of Yorkshire, Cumberland, Durham, Northumberland, and Westmoreland, contain rich galena deposits, and, although the mines are closed, many are in a position to reopen when circumstances are more favourable, for their working.

In Derbyshire, some 400 mines are presently engaged in raising the ore from the mountain limestone formation; the bulk of the workings are, however, small, the yearly output of each mine being a few tons only.

The extensive lodes of the Laxey and Foxdale mines, in the Isle of Man, have long been known. The former is carried to a depth of 1740 feet, and has reaped a rich harvest of wealth for many years, and the latter has returned to its owners a profit of nearly two millions sterling. The ore deposits are mainly galena, containing 40 to 78 per cent. lead, and the low-grade ores are concentrated, before smelting, by dressing and washing. The metallurgical operations are carried on in the reverberatory or Flintshire furnace solely, or, as in Cumberland, Durham, and Northumberland, by a preliminary roasting in the reverberatory, and then by reduction in low square blast furnaces of the Scottish hearth type, the loss by both processes averaging 6 per cent. lead.

Scottish lead-mining may be considered as non-existent. Formerly, the counties of Ayr, Argyle, Kirkcudbright, Lanark, and Dumfries produced a varying quantity of ore, but for many years the mines have been abandoned. Leadhills, in Lanarkshire, was the principal seat of the industry, the mines and works being carried on by the Hopetoun family or their lessees. The workmen employed were divided into four classes—miners, labourers, washers, and smelters, the first being engaged exclusively in getting the ore, or in forming the necessary shafts and adits. In the latter case they were paid according to the number of fathoms cut; in the former, by the number of tons smelted

lead realised from the ore; the rate of payment also varied according to the nature of the rock and the richness of the vein. The miners descended, not by ladders, as in some shafts, but were let down and pulled up by a rope attached to a windlass, worked by their comrades. In descending, the miner first made a loop on the end of the rope, and the right leg thrust through, the rope being grasped between the left arm and side, leaving free the hand to hold the candle inserted in a ball of clay, while the right hand was used to prevent him from coming into contact with the rocky sides of the shaft.

Deeper and consequently more expensive workings, the want of machinery for raising the water, which could no longer be carried off by the usual channels employed, along with the low price of lead, made their abandonment necessary.

During the decade 1881–1890 the whole of the produce of the Leadhill mines has been derived from the portions of ore contained in the “rubbish” of the old workings, which was thrown aside as unworthy of attention during more prosperous times, with the occasional addition of small knots of ore, limited in their extent, which had been accidentally missed.

The Irish lead mines have been closed for many years. In 1861 the industry was of some importance, mines being worked in five counties. At the close of 1878 two mines only were in working—one at Newtownards in County Down, and the other at Luganure, County Wicklow. In that year the value of the products of these mines was £14,090, and in 1883 only £3397 was realised, and this amount was further reduced, during 1885, to £790. In 1886 only the Luganure mine was raising ore, the value of the silver and lead being £1928, and three years later (1889) the value of the silverized lead had increased but slightly. Since that period the mine has been closed. The ore is an argentiferous

galena containing 35 to 75 per cent. lead, and, before smelting in the reverberatory furnace, the low-grade class is brought to a strength of 60 per cent. by dressing and washing.

Lead-mining in Ireland is not profitable; the foot and hanging walls which enclose the lead veins are of granite, and their removal adds greatly to the cost of running the mine. Then, again, the deposits are very "bunchy," and the intervening ore is so very lean that its reduction is not possible at a profit.

Mexico.—This country possesses extensive deposits of argentiferous galena and cerusite. They are found at Lomode-Toro, State of Hidalgo, and also in the State of Coahuila, at a depth of 300 to 400 feet. The smelting of the dressed ores is done in water-jacket furnaces of 20 to 30 tons capacity, and the charge is mixed with coke, lime, iron oxide, and silica to effect the reduction, the proportions varying to meet the requirements of the ore. The raw ores contain from 20 to 60 per cent. lead, and the smelting yields 85 to 92 per cent. The argentiferous "pig" lead produced, is mainly exported to the United States for further treatment.

Turkey.—The Empire raises but a small quantity of galena, and that principally by the Asia Minor Mining Company, at Lidjessy, near Sivas. The mining is carried on by day-levels driven into the hills. The ore obtained is of poor quality (9 to 12 per cent. lead), which after dressing is exported.

Australia—New South Wales.—Rich silver-lead deposits are found at the Broken Hill mines in this colony, the average percentage of lead in the silver ores being 55. Up to the end of 1889 the total net value of silver, silver-lead and ore produced, realised £27,882,997, and the output value for 1899 was £2,070,657, the larger portion being won from the Broken Hill mines. This amount would have been considerably increased, but that the transfer of the

smelting operations in that year, from Broken Hill to Port Pirie, South Australia, of necessity limited their output.

Queensland.—The silver-galena ores of Queensland are found at a depth of about 300 feet, and average, when untreated, 20 per cent. lead. After dressing, they are smelted in the water-jacket furnace, and the yield is 88 per cent. of the lead in the dressed ore, the loss being due to volatilisation and unrecovered metal in the slags. As in New South Wales, the value of the ore depends entirely on the silver contents.

South America — Argentine. — In the interior of the country, since the days of the Spanish conquerors, there have been spasmodic efforts to develop the mining, but with little or no return. The search, however, was made for gold and silver, and little attention was paid to the extensive lead ore deposits which are now known to exist.

Canada, in the Kootenay district of British Columbia, and Greece, in the mining centre of Laurion in the province of Attica, are making rapid strides in developing their mineral resources, and in the future will take an important part in the world's production of lead.

CHAPTER III.

CHEMICAL AND PHYSICAL PROPERTIES OF LEAD.

THE metal has a bluish-grey colour, is fusible at 330° C. (626° F.), and has a specific gravity of 11.358. English commercial lead is nearly pure; the small proportion of impurities present consist mainly of antimony, zinc, and iron. The following represents the composition of some brands of English manufacture:—

	1	2	3
Lead	99.994	99.971	99.948
Silver	trace	trace
Iron	0.003	0.007
Zinc	0.004	0.017	0.019
Antimony	0.002	0.005	0.022
Copper	trace	0.004
	100.000	99.996	100.000

The impurities in lead affect the physical and chemical properties of the metal in proportion to the amount present. They give to the metal that peculiar property termed "hardness," which renders it unsuitable for many uses in the arts. The malleability and ductility are reduced, and when in the form of sheet lead for use in the lining of vessels, vitriol chambers, etc., they lower the resistance of the sheet to acid vapours, the surface becoming corroded.

The "hardness" of lead is removed and a "soft" metal produced, by the process of calcination, the impurities being

practically removed by conversion into oxides, which form a scum on the surface of the molten lead.

Strong acids act very differently on lead. Nitric acid dissolves it, even in the cold, forming nitrate of lead, while hydrochloric acid has practically no action; the two mixed together, as aqua-regia, converts the metal into chloride. Sulphuric acid, when boiling only, feebly attacks lead with the formation of sulphate. Arsenic or arsenious acid unites with the metal, yielding arsenite or arsenide of lead.

Lead, unlike many other metals, is not sonorous when struck, and is a poor conductor of heat and electricity. When it is cut or scraped, a bright lustrous surface is seen, which rapidly becomes dim through the formation of a thin film of oxide of lead. In a perfectly dry and pure atmosphere, Miller states that it undergoes no change, but when exposed to the joint action of pure air and pure water, *i.e.* water boiled free of its carbonic acid and oxygen, mechanically held, the surface of the metal becomes oxidised to oxide of lead, which ultimately becomes transformed into a film of hydrated carbonate of lead, by the absorption of the carbonic acid gas from the air. This salt is only soluble to the extent of $\frac{1}{100}$ th of a grain per gallon. When, however, the water retains its carbonic acid, the film is dissolved and fresh surfaces of the metal are exposed, to undergo, first, the formation of oxide, and then the hydrated carbonate. The latter can only be formed after the oxidation of the lead. These facts bring into view the great danger, from a sanitary standpoint, of the use of lead in domestic utensils, storage cisterns, etc.

The water supply of our towns is charged with wholesome oxygen and carbonic acid, which in continual contact with the metallic surface forms, and then dissolves, a poisonous white lead, producing in course of time all the painful symptoms of lead colic.

The cisterns of all houses used for water storage should never be lined with sheet lead, but with slate, and all leaden pipes coated internally with tin, to resist the action of air and water. In the vessels used in the preparation of beverages, the same danger exists, if they have an internal lining of lead.

Lead has considerable power of affinity or attraction, but some of its compounds can be dissociated by the chemical force of a stronger metal. This can be illustrated by means of a salt of lead and metallic zinc. If 28.4 grms. (1 oz.) of acetate of lead are dissolved in a litre of water, and a piece of zinc suspended in it, the metal will shortly be covered with a grey coating, from which brilliant metallic spangles will shoot forth, somewhat in the shape of a tree. These are pure lead, and the phenomenon is known as the "lead tree."

The effect thus produced is due to the superior affinity of the zinc for the acetic acid combined with the lead, which causes the two metals to interchange places.

Uses of Lead.—Owing to its softness, plasticity, and low fusibility, the uses of lead may be said to be multifarious. For roofing purposes and the lining of cisterns and chambers for manufacturing work, large quantities are consumed. In the making of piping, white lead, and the various compounds of lead, such as the nitrate and acetate, for the dyeing and printing industries, also in pottery and glass work, lead in the metallic state, or oxidised as litharge, is extensively used. The various commercial alloys include a large proportion of the metal, and it is also used in the manufacture of bullets and small shot, where great momentum confined to a small compass is required. Further, the properties of lead make it valuable in other branches of work, and its manufacture may be truly said to "minister directly to the necessities and luxuries of human existence."

Welding of Lead.—Lead joints are generally made by soldering or burning with the oxyhydrogen flame. In 1896 Blondel brought out an ingenious method, by which the joints may be welded instead of soldered or burnt. For this purpose, the surfaces to be joined, are carefully cleaned, and between them is placed a thin layer of lead amalgam. On passing an ordinary soldering iron along the line of junction, the mercury of the amalgam is vapourised, and the lead set free in an exceedingly finely divided state, fuses, and then unites the two surfaces together. The joint is said to be more durable than when made in the usual way.

Alloys of Lead.

Lead mechanically unites in varying proportions by simple fusion with tin, antimony, arsenic, bismuth, copper, zinc, phosphorus, and other elements, forming a series of mixtures, termed alloys. Many of these alloys are very important, and are largely used in the arts.

The following table by Stillman, represents the percentage composition of the leading alloys used for bearings and other engineering purposes:—

Alloy.	Iron.	Tin.	Antimony.	Lead.	Copper.	Zinc.	Bismuth.	Phosphorus.
Babbitt metal . . .	45·5	13·00	40·00	1·50
Anti-friction metal . . .	40·00	5·00	55·00
Tobin bronze . . .	0·20	0·90	...	0·40	61·20	37·30
Phosphor bronze	10·00	...	9·50	79·70	0·80
Deoxidised bronze . . .	0·20	12·40	...	2·27	82·67	2·45	...	0·005
Magnolia metal	4·75	15·00	80·00	0·25	...
Rose metal	22·90	...	27·10	50·00	...
Camelia metal . . .	0·55	4·25	...	14·75	70·20	10·20
Ajax metal	10·98	...	7·37	81·28	0·37
Car box metal . . .	0·61	...	14·38	84·33	...	0·68
Parson's white metal	86·00	2·00	2·00	2·00	7·00
"B" alloy P.R.R.	8·00	...	15·00	77·00

Lead alloyed with antimony and tin forms stereotype and type metals—

	Lead.	Antimony.	Tin.
Stereotype metal	84.25	13.50	2.25
Type metal	70	25	5

The antimony is added to harden the alloy, while the tin gives it the necessary coherence. When melted with tin alone, and in certain proportions, lead forms pewter and solder.

The former, in 100 parts, is composed of—

Tin	80
Lead	20

This proportion yields an alloy of great tenacity and of a lower melting-point than that of the metals individually, in addition to its non-liability to corrosion when used for drinking purposes. An increase in the amount of lead, however, renders the alloy liable to be attacked by even weak organic acids, and its use then becomes dangerous.

The latter is made in three forms—common, coarse, and fine solder. The following are the proportions used :—

	Lead.	Tin.	Melting-Point.
Common solder	50	50	385° F.
Coarse solder	66.65	33.35	379° F.
Fine solder	33.35	66.65	372° F.

Similar to pewter, the melting-points of these alloys are lower than either of their composing metals.

The alloy of lead and arsenic is used in the manufacture of rifle and shell bullets and small shot.

The former also contains a small proportion of antimony to increase the penetrative power.

In the manufacture of small shot, the arsenic used amounts to about 40 lb. to every ton of the metal, and has the physical effect of securing to the molten lead a spherical form, when dropped into water from a perforated vessel. The manufacture is carried on in high buildings, termed shot towers, the arsenical lead being allowed to fall from perforated wrought-iron dishes, placed at the top of the building, into a layer of water at the bottom; the fall (100 to 150 feet, according to the size of shot prepared) is required to enable the particles to become chilled and assume the spherical shape before entering the water. On complete cooling, the shot are dried, sifted into different sizes, and then polished with plumbago in a revolving cylinder.

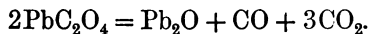
Compounds of Lead.

Oxides.—Lead combines with oxygen, forming five oxides, namely—

Suboxide of lead	Pb ₂ O.
Protoxide „	PbO.
Red oxide „	Pb ₃ O ₄ .
Sesquioxide „	Pb ₂ O ₃ .
Peroxide „	PbO ₂ .

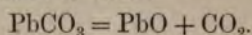
The protoxide also unites with water, forming the hydrate or hydroxide of lead, PbO.H₂O or PbH₂O₂.

Suboxide of Lead.—The suboxide is prepared by carefully heating oxalate of lead in a closed vessel, the following reaction taking place:—



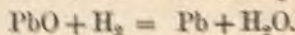
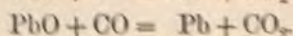
The resulting black powder is rapidly converted into hydrate on exposure to air. Dilute acids convert it into protoxide, which combines with the acid used and finely divided metallic lead.

Protoxide of Lead.—This oxide can be obtained pure by igniting—not to fusion—basic nitrate, carbonate or oxalate of lead, in a platinum crucible. The following is the equation when the carbonate is used:—

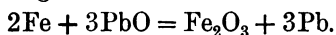


The oxide has a dull lustre, and a colour varying from sulphur to orpiment yellow. The specific gravity is 9.36 at 4° (Joule and Playfair), and it is reduced to the metallic state by carbonic oxide (CO) at 100°, and by hydrogen at 310° (Roscoe and Schorlemmer). According to Watts, the protoxide is both dimorphous and amorphous, and crystallizes in pale yellow rhombic octahedrons and cubes and regular dodecahedrons. It also occurs as a red amorphous powder. The crystalline form can be obtained by (1) the slow cooling of the protoxide after fusion, (2) by fusion with hydrate of potassium, and (3) by treating with potash or soda ley. If the ley is brought to the boil at a strength of about 40° B., and then moderately saturated with the protoxide, the liquor on cooling deposits red scales or crystals soluble in acetic acid, fully showing that the protoxide under certain conditions may partake of a red colour without any admixture of the higher oxide (minium). Watts states that these red crystals are also produced when the protoxide is moistened with water to form the hydrate of lead, then dissolved to saturation in a boiling soda ley of 40–41° B., and afterwards cooled.

The protoxide has a great affinity for acids, forming well-known neutral and soluble salts, the most important being the nitrate and the acetate. It is rapidly reduced to the metallic state at a dull red heat, by carbon, hydrogen, and carbonic oxide, as seen in the following equations:—



On heating with copper, zinc, or iron in a finely divided state, it acts as an oxidising agent, converting these metals into oxides, and becoming reduced to metallic lead : for example—



The protoxide when heated to redness loses its yellow colour, and assumes a reddish-purple tint ; the original shade is, however, restored, on cooling the heated mass.

On boiling it with milk of lime and settling, a liquor is yielded which has found a use in hair-dyeing, etc. Hair-dyes containing lead in any form should be avoided.

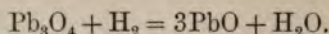
In commerce the protoxide is technically known as litharge and massicot. The two products have exactly the same composition, but differ as regards their colour and physical properties. Their manufacture is described under the heading of Litharge.

Red Oxide.—This oxide occurs native to a limited extent in various lead-mining districts. It was known and described in the early ages by Pliny, Dioscorides, and others. It is prepared on the small scale by heating protoxide of lead with 1 part potassium chlorate and 8 parts of potassium nitrate (saltpetre) in a platinum crucible. At the temperature of dull redness the minium begins to form at the edge of the crucible, and, on cooling, the crucible and its contents are boiled in a weak potash liquor, to dissolve out any protoxide left. On settling and running off the supernatant liquor, the minium appears as a bright red powdery substance. Watts produces a minium by boiling the peroxide of lead with aqueous plumbate of potassium, or 1 part of the peroxide with 5 parts of nitrate of lead dissolved in water, and then sufficient quantity of weak potash or soda added, to redissolve the hydrate of lead first precipitated, and until a brown-red mixture of minium and peroxide is produced. This is digested with oxalic acid, which decomposes the peroxide without acting on the minium.

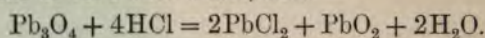
In the cold, the shade is bright red, but, on heating, it changes to a deep violet tint. Minium has a composition of—

Lead	90.60
Oxygen	9.40

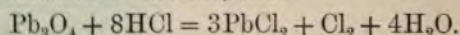
and a specific gravity of 8.62 (Karsten). Many oxidisable bodies convert it into protoxide of lead. With hydrogen also, it yields protoxide and water, as seen from the following equation :—



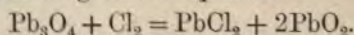
With hydrochloric acid, minium is converted into chloride and peroxide of lead and water, thus—



If the proportion of acid is increased, the whole of the lead is converted into chloride, thus—



The action of chlorine water also yields chloride and peroxide of lead, according to the equation—



Minium is soluble in phosphoric and arsenic acids, forming salts of the peroxide. Watts states that it dissolves in nitric, dilute sulphuric, and likewise by weaker acids, being resolved into protoxide and peroxide of lead, the former yielding an ordinary lead salt, while the latter remains undissolved.

The manufacture is described under the heading of Minium, or Red Lead.

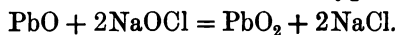
Sesquioxide of Lead.—This oxide may be considered as a combination of monoxide and dioxide, as it is resolved by acids into these two oxides. It is prepared (1) when a solution of sodium hypochlorite is carefully added to a caustic potash solution of lead oxide (Winkelblech), or (2) when a solution of minium in acetic acid is precipitated by a very

dilute solution of ammonia (Roscoe). It is a reddish-yellow powder, with a composition of—

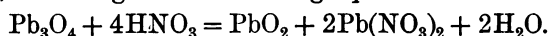
Lead	89.66
Oxygen	10.34

The sesquioxide is rapidly reduced to the protoxide by the action of oxalic and formic acids, and is also soluble in dilute nitric and acetic acids, forming soluble salts of lead, along with peroxide.

Peroxide of Lead.—This oxide, sometimes termed brown or puce lead, is found native as plattnerite, in the form of black-coloured, six-sided prisms. Böttger prepares it by acting on protoxide of lead with sodium hypochlorite, thus—



It is also a result of the action of dilute nitric acid on minium, according to the following equation:—



Ozone, acting on the protoxide of lead, also yields the peroxide, by absorption of oxygen.

The peroxide has a strong oxidising action, and, according to Vanquelin, when ground with one-sixth of its weight of sulphur, it takes fire, burning with a brilliant flame, forming in the first instance sulphide of lead, and then the sulphate. Some organic acids—gallic acid, for example—also ignite in contact with it.

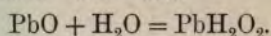
Peroxide of lead has a great affinity for the alkaline bases, acting the part of a weak acid towards them, hence the term “plumbic acid” by which it is sometimes known. These compounds are of definite composition, the potash salt having the formula of $\text{K}_2\text{O} \cdot \text{PbO}_2 \cdot 3\text{H}_2\text{O}$, and is prepared by fusing the peroxide with excess of potash, dissolving the fused mass in water, filtering, and then evaporating *in vacuo*. Fremy says the crystals so produced, have a rhombohedral form.

Peroxide of lead, prepared by any of the above methods, has a brown colour, and is quickly decomposed by heat, which liberates part of its oxygen, converting it into minium or protoxide. The composition is—

Lead	86.67
Oxygen	13.33
	<hr/>
	100.00

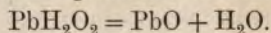
A mixture of peroxide and nitrate of lead is employed in the manufacture of lucifer matches.

Hydrate or Hydroxide of Lead.—The hydrate is a combination of the protoxide with water—



It is prepared on the small scale by adding an excess of ammonia to a saturated solution of acetate of lead, the hydrate being precipitated as a white crystalline powder, the crystals, as seen under the microscope, having an octahedric form.

The hydrate is to some extent an unstable body, for at 130° it loses a portion, and at 145° the whole of its water, being reconverted to the protoxide of lead—



Salts of Lead—Acetate of Lead.—This salt is familiarly known as sugar of lead, from its sweetish taste and close resemblance to sugar. In the early ages, Geber was conversant with it, and gave a description of its preparation and properties. The acetate is placed on the market as a white or brown product, the difference in the two qualities being due to the quality of acid used in their manufacture. The white acetate has a value of £24, 10s., and the brown £19 per ton.

The white acetate is prepared from litharge and good quality acetic acid, the proportions used being 1 ton litharge to 23 cwt. of acid (45 per cent. strength). The manufacture

is carried on in large wooden vats, lead-lined, termed the dissolving vats, and at the bottom of each is placed a steam coil for boiling purposes. They are arranged on a platform, so that the treated liquors can be run direct into a series of evaporating vats, lead-lined, and fixed below the level of the platform.

The proportion of acid is first run into each of the dissolving vats, and then the required amount of litharge slowly added, with constant stirring. When solution has taken place, the liquors are brought to the boil, which brings to the surface any impurities as a scum, which is skimmed off. They now flow through shallow filters to the evaporating vats below, and are concentrated by the aid of steam coils to a density of 1.5, and from thence pumped to the "crystallizers," which are shallow lead-lined vessels, each 4 feet long, $2\frac{1}{2}$ feet broad, and 8 inches deep. On slow cooling, the acetate crystallizes out, and the crystals are removed to wooden racks, to drain from any mother liquor, and afterwards broken up for the market.

In the manufacture of the brown acetate, pyroligneous acid is used in place of the pure acetic acid. After dissolving in the vats, the resulting liquors are very muddy, and consequently require to settle. On clearing, they are run to a large lead-lined pan, and heated to boiling by a coil. A further settling is then allowed, and the clear but dark-coloured liquors thence flow to the evaporating pans, and are concentrated till crystallization commences. A proportion of water is now added, causing the impurities to rise to the surface. The liquors are skimmed, and again evaporated to the crystallizing point. This is repeated, if the liquors remain muddy after concentration. The crystallization and drainage of the formed crystals are conducted in the same manner as in the white acetate. The yield of brown acetate is about 1 ton for every $13\frac{1}{2}$ cwt. litharge used.

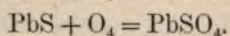
Acetate of lead crystallizes with 3 molecules of water, having the formula $\text{Pb}2(\text{C}_2\text{H}_3\text{O}_2)3\text{H}_2\text{O}$. It is soluble in

alcohol, and also in its own weight of cold water. On exposure to a dry atmosphere, the salt loses its water of crystallization, and thence absorbing carbonic acid is converted into carbonate of lead. In a state of fusion, it decomposes with the formation of acetone, and leaving a residual mass of finely divided metallic lead and carbon.

Acetate of lead is used in medicine under the name of Goulard extract or lead vinegar, the preparation being formed by digesting litharge in a warm solution of lead acetate. For technical purposes, large quantities of sugar of lead are used in calico printing, and in the preparation of the acetates of iron and alumina, for use in dyeing.

Sulphate of Lead.—When a soluble lead salt is treated with sulphuric acid, a white precipitate is formed, which on washing and drying has the formula PbSO_4 .

Sulphate of lead is also found native as anglesite, and in combination with other salts as linarite, caledonite, and leadhillite. On the large scale, it is prepared by volatilising sulphide of lead (galena) on a coke bottom, and then oxidising to sulphate with a blast of air, the reaction being—



It is a white crystalline powder, practically insoluble in water, but freely soluble in acetate of ammonium. Hydrochloric acid slowly converts it into chloride of lead, the hot solution, on cooling, depositing needle-shaped crystals of the chloride.

Sulphate of lead is volatile without decomposition at a red heat; when mixed with powdered charcoal and heated to dull redness, it is resolved into sulphide, oxide, or metallic lead, according to the proportion of carbon present. Sulphate of lead, unlike the basic carbonate, does not saponify with linseed oil, the combination being a mechanical and not a chemical one.

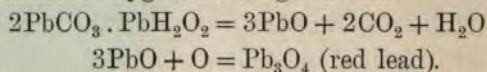
The manufacture is described under the heading of Sulphate of Lead.

Carbonate of Lead.—This compound exists naturally, as the crystalline cerusite, the mineral being a neutral anhydrous carbonate. Carbonate of lead forms both a neutral and a basic salt. The former is valueless as a pigment; the latter is the basis, *par excellence*, of a paint requiring whiteness, permanence, and covering power. The basic carbonate, in form but not in composition, has been known for over 2000 years. Theophrastus, about 300 B.C., describes the preparation of a white body from vinegar and lead, and Pliny also, in the first century, refers to a similar product. It was introduced by the Dutch or Flemish people 300 years ago from Italy, where it had been employed many centuries before. As in the modern methods of manufacture, the production of a white pigment in the early ages depended on the action of vinegar on lead. The primary essentials of the art of making have never changed during the many centuries' knowledge of its value, and to-day vinegar and lead yield the most durable, permanent, and economical of white pigments, as in the dim ages of the alchemists. As before mentioned, the native carbonate is a neutral anhydrous body with the formula PbCO_3 ; on the other hand, the basic salt requires preparation, and may be produced on a small scale by treating a soluble lead salt with a solution of sodium carbonate. The white precipitate, on washing and drying, has the composition of either of the following formulæ, according to the temperature and concentration under which it is produced (Payen):—

	Parts per 100.		
	Protoxide of Lead.	Carbonic Acid.	Water.
$2\text{PbCO}_3 \cdot \text{PbH}_2\text{O}_2 =$	86.38	11.31	2.31
$3\text{PbCO}_3 \cdot \text{PbH}_2\text{O}_2 =$	85.66	12.62	1.72
$5\text{PbCO}_3 \cdot 3\text{PbH}_2\text{O}_2 =$	86.73	10.65	2.62

The qualities of commercial white lead, made by the "Dutch" process, and approximating most nearly to the formula $2\text{PbCO}_3 \cdot \text{PbH}_2\text{O}_2$, may be considered as standing the highest for durability and covering power.

Basic carbonate of lead is totally insoluble in pure water. It is soluble, however, in water impregnated with carbonic acid, and also in solutions of potash or soda. Sulphides of the alkalis and sulphuretted hydrogen, convert it into a black sulphide of lead. Sulphuric, hydrochloric, and acetic acids, dissolve it with effervescence, forming the sulphate, chloride, and acetate of the base respectively. At a temperature of dull redness, the basic carbonate first loses its water of combination, then the carbonic acid, being ultimately converted into protoxide of lead, which, if the temperature is continued, absorbs oxygen, forming red lead—



According to the method of preparation, the basic carbonate of lead exists as a spongy transparent globular powder, or is crystalline, and on this difference in the physical form depends its value as a pigment.

A crystalline basic carbonate, when ground with linseed or other oil, practically absorbs but little of the oil, and the resulting white paint lacks both covering power and permanence. On the other hand, the globular form, when so treated, takes up the oil, somewhat as a sponge absorbs water; and to this action, which is a chemical one, is attributed its greater body and durability. To this variety belongs the Dutch corroded lead of commerce. Only this form of the basic carbonate unites with the fatty acids of certain oils, yielding true lead soaps. With a crystalline basic carbonate, or any other white pigment of lead, this chemical action does not take place, the combination with the oil being only a mechanical one.

The manufacture is described under the heading of Dutch White Lead.

Nitrate of Lead.—The neutral salt is prepared by dissolving litharge in dilute nitric acid at a boiling heat, and then evaporating the solution to the crystallizing point, the nitrate of lead separating out in large octahedrons, sometimes transparent, although generally white and opaque. The crystals are anhydrous, soluble in eight times their weight of cold water, and also are dissolved by saturated solutions of saltpetre and nitrate of barium.

At a red heat, nitrate of lead is broken up, yielding oxygen and nitric peroxide, and leaving the yellow protoxide of lead.

Diplumbic nitrate, $2\text{PbO} \cdot \text{N}_2\text{O}_5$, is a basic nitrate of lead produced by boiling the neutral salt with white lead and water. The crystals have a sweet astringent taste.

Triplumbic nitrate, $3\text{PbO} \cdot \text{N}_2\text{O}_5$, prepared by precipitating the normal salt with excess of ammonia, exists in needle-shaped crystals, but sparingly soluble in boiling water.

The basic salts find no use in the arts, and are of interest only to the chemist.

Chloride of Lead.—This compound is found native as cotunnite, in the form of trimetric crystals, the mineral having a white colour and a specific gravity of 5.23. The composition is—

Lead	74.552
Chlorine	25.448
							<hr/>
							100.000

It is prepared on the small scale by adding hydrochloric acid to a soluble lead salt, or by boiling the protoxide of lead with water, in which hydrochloric acid is dropped, so long as the resulting chloride of lead continues to dissolve (Watts). In hot water, chloride of lead is completely soluble; on cooling, however, it separates out in needle-shaped crystals. It is

moderately soluble in weak, and practically insoluble in strong, alcohol. When heated to redness in contact with air, chloride of lead absorbs oxygen and forms the series of compounds termed oxychlorides. It may be sublimed by heating out of contact with air, the fused mass on solidifying forming the product termed horn-lead. According to Göbel, when heated in a stream of carbonic oxide, phosgene gas (CoCl_2) is produced with a separation of metallic lead. Chloride of lead is not used in the arts.

Phosphate of Lead.—Phosphate of lead mixed with chloride is found at Leadhills in Scotland, and in Derbyshire, Cornwall, Yorkshire, and other places, as a yellowish-green mineral, with the formula $3(\text{P}_2\text{O}_5 \cdot 3\text{PbO}) + \text{PbCl}_2$. It is known to mineralogists as pyromorphite, and contains—

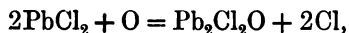
Chlorine	2.52	} Chloride of lead.
Lead	7.39	
Phosphoric acid	15.59	} Phosphate of lead.
Oxide of lead	74.50	
<hr/>		
100.00		

On the small scale, it is prepared by adding a solution of sodium phosphate to a soluble lead salt, the precipitate of phosphate of lead separating out as a white crystalline powder. The phosphates of lead constitute a series of compounds, known as (1) orthophosphates, (2) metaphosphates; they are, however, not used in the arts.

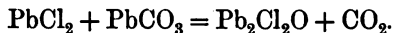
Oxychlorides of Lead.—The following combinations of protoxide of lead with chloride of lead are known:—

- (1) $\text{Pb}_2\text{Cl}_2\text{O} = \text{PbCl}_2 \cdot \text{PbO}$.
- (2) $\text{Pb}_3\text{Cl}_2\text{O}_2 = \text{PbCl}_2 \cdot 2\text{PbO}$.
- (3) $\text{Pb}_4\text{Cl}_2\text{O}_3 = \text{PbCl}_2 \cdot 3\text{PbO}$.
- (4) $\text{Pb}_4\text{Cl}_6\text{O} = 3\text{PbCl}_2 \cdot \text{PbO}$.
- (5) $\text{Pb}_6\text{Cl}_2\text{O}_5 = \text{PbCl}_2 \cdot 5\text{PbO}$.
- (6) $\text{Pb}_8\text{Cl}_2\text{O}_7 = \text{PbCl}_2 \cdot 7\text{PbO}$.

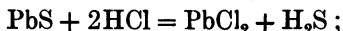
(1) $\text{Pb}_2\text{Cl}_2\text{O}$.—This oxychloride is found native as matlockite. It is prepared on the small scale by igniting the chloride of lead in contact with air (Watts)—



or by fusing the chloride and carbonate of lead together, carbonic acid gas being evolved (Döbereiner)—



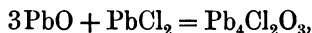
Pattison prepared this compound, as a pigment, on a manufacturing scale by heating finely divided galena with hydrochloric acid, in a large vat provided with a hood for carrying off the deleterious gases, the reaction being the formation of chloride of lead with evolution of sulphuretted hydrogen—



any silver, copper, or iron at the same time being converted into chlorides. On cooling, the chloride of lead was deposited in crystals, along with the chloride of silver, and from this residue any soluble chlorides of iron and copper were easily washed by cold water. The residue was now transferred to a large vat of boiling water, which dissolved the chloride of lead, and leaving a small residue of chloride of silver and any silicious matter; and from this, the silver was separated by drying and then melting the residue with lime. The hot solution containing the chloride of lead was then treated with thin hydrate of lime, in quantity sufficient only to neutralise half of the hydrochloric acid present, the precipitate of oxychloride of lead formed, being dried and ground in oil, as a substitute for white lead.

(2) $\text{Pb}_3\text{Cl}_2\text{O}_2$.—Interesting only as a mineral. It occurs native as mendipite.

(3) $\text{Pb}_4\text{Cl}_2\text{O}_3$.—This compound is prepared by fusing chloride and protoxide of lead—



and also as a hydrate $\text{Pb}_4\text{Cl}_2\text{O}_3 \cdot \text{H}_2\text{O}$, by precipitating basic acetate of lead with common salt, or by decomposing a

solution of common salt with protoxide of lead (Watts). This oxychloride in the anhydrous state forms a yellow powder, which has been used to some extent as a pigment. The hydrate also has been prepared on the large scale, by Pattison, for use as a substitute for white lead.

(4) $\text{Pb}_4\text{Cl}_6\text{O}$.—This oxychloride has no commercial importance; it is prepared on the small scale by fusing together a mixture of 4 parts chloride with 1 part protoxide of lead.

(5) $\text{Pb}_6\text{Cl}_2\text{O}_5$.—On fusing 5 parts of protoxide with 1 part chloride of lead, it is produced as a deep yellow powder.

(6) $\text{Pb}_8\text{Cl}_2\text{O}_7$.—This oxychloride is formed by fusing 10 parts protoxide of lead with 1 part sal-ammoniac. It formerly had a commercial value, and was known as cassel yellow.

Sulphides of Lead.—Lead unites with sulphur, forming three compounds, namely, the subsulphide, tetrasulphide, and the protosulphide of lead. While little is known of the constitution and properties of the two former, the latter is of especial importance, as the basis of galena ore. On a small scale, it is formed by treating a soluble lead salt with sulphuretted hydrogen, or by heating to dull redness lead filings and sulphur. Protosulphide of lead is acted upon by strong acids, hydrochloric acid converting it into chloride of lead with liberation of sulphuretted hydrogen, and fuming nitric acid oxidises it to sulphate of lead.

CHAPTER IV.

DRESSING OF LEAD ORES.

GALENA when mined is generally found mixed in more or less proportions with pyrites (iron and copper sulphides), blende (zinc sulphide), calamine (zinc carbonate), light spar (carbonate of lime), heavy spar (sulphate of barium), sandstone, quartz, and other silicious matters, according to the strata in which the ore is found; and to remove these ingredients, and thus concentrate the ore and render it fit for smelting, the operation of "dressing" is carried out. This method of treatment consists of a washing of the crushed ore, the particles thereafter arranging themselves according to their specific gravities. If a mixture of a pure galena and quartz crushed to a similar state of division, were equally washed through a sieve into a receptacle beneath, it would be found that the bottom layer would contain the galena, and the surface layer the lighter quartz. Or, if a mixture of the two were deposited at the head of an inclined plane and washed with water, the stream would carry the quartz farther than the galena and thus allow the two bodies to deposit themselves, the heavier mineral nearest the end of the plane, whilst the lighter quartz would be carried farther on. This difference in deposition is solely due to the variation in the specific gravities of galena and quartz, the former being 7.5 and the latter only 2.6. In the first example, the velocity of fall after a lapse of one second, according to P. von Rittinger, would be 16.309

inches for the heavy galena and only 8.031 inches for the lighter quartz, consequently the lead would be first deposited; in the second, the heavy specific gravity of the galena would offer a greater resistance to the flow of water than the lighter quartz, and thus be carried a lesser distance.

On the large scale, the ore first undergoes a crushing process, being resolved into fine particles for the better separation of extraneous matter in washing. In the olden days of lead-mining, this was done by means of a "bucker" and "drag,"—the first being a kind of hammer with a long shaft or handle, called the "brashing bucker"; and the other, a strong toothed iron rake, to drag off or separate the less from the more crushed parts, after the "brashing bucker" had been used. This laborious method gave way to a form of the modern stamping mill, consisting of three strong wooden posts, perpendicularly placed, and working in guides attached to the framework of the mill. The posts were actuated by three cams fixed to the horizontal shafting, and at their lower ends were affixed shoes or stampers of cast-iron, which worked in iron mortars resting on blocks. At the back of each mortar were placed a series of holes for the crushed ore to pass through by the aid of a current of water. The number of drops made by each post were 20 to 30 per minute.

In the modern mill as many as 100 head of stamps are used in a battery, and some are driven by compressed air, or steam in the form of a steam hammer, the number of drops each minute ranging from 80 to 90, and crushing 100 to 120 tons of rock ore in twenty-four hours.

The crushed ore is washed through a screen placed in the lower half of each mortar, and forms a pulpy mass for further treatment. When the ore is mixed with large pieces of rock or mineral, it undergoes a preliminary breaking, before enter-

ing the mill, by passing through a "stone-breaker" to reduce the lumps to a size convenient for stamping.

Washing the Crushed Ore.—The washing of the ore, to effect a separation of extraneous matter, is of vital importance to the smelter, for on its cleanliness depends the successful working of his furnace and the quality of lead yielded. The presence of any appreciable quantity of stone or quartz prevents vitrefaction, the hearth becoming choked, and the produce greatly wasted; on the other hand, light spar is the most harmless ingredient that can be left in the ore, for, at a moderate smelting heat, it digests into a very light and distinguishable slag. With heavy spar, which is a close, opaque, and extremely refractory substance, the opposite takes place, heavy spar being infusible even at a high temperature. Copper and iron pyrites and all antimonial ores, when present, are very pernicious, the latter rendering the lead hard—a property which makes it unfit for many uses in the arts; whilst the smallest amount of copper renders the "pig" lead produced quite useless for the manufacture of white lead. A careful washing, then, is a necessity, and, as before mentioned, the art depends entirely on the differences in specific gravity of the ingredients of the crushed ore.

Various mechanical contrivances are used for the purpose, amongst which may be mentioned: The buddle, the syphon separator, the jiggers, the shaking table or frame, and the magnetic separator.

The buddle has long been employed for washing lead ores, and several forms of it are in use: for instance, the trunk buddle, which consists of a flat chest or trunk, 9 feet long, 3 feet broad, and 10 inches deep, supported on wooden stays, and having an outlet 8 inches in width at one end for the water; to this or lower end, is connected a passage to a wooden box 18 inches in length and 14 inches

in width and depth. The trunk and passage are fixed at an inclination to the box.

The crushed ore is shovelled into the trunk at the head, and subjected to a current of water, which carries the lighter matter over to the box, leaving the heavier or richer portion at the end of the trunk, which is dug out in sections, dried, and made ready for smelting.

The round buddle is either made concave or convex; in the former, the dip being to the centre, the crushed ore is fed round the circumference, and washed with a stream of water, which carries the lighter matter to the middle of the washer, where it falls through an opening. With the convex form, the working conditions are reversed, the feed being in the centre, and the circumference receiving all the tailings, of little or no value to the smelter.

The circular buddle, devised by Herr Hundt, and described in the *Mining and Smelting Magazine* (1862), is a very effective form of the concave washer.

In Fig. 1, A represents the end of section of the slime or pulp trommel, over the outside of which the launder B discharges clean water for the washing. C is the inflow for the slimes, delivering them to the central trough D, which is fitted concentric with and is supported by the vertical axis E. This also carries the four arms F F F F, which are connected to and revolve with the central trough. The wooden bars G G are connected with the four arms by vertical sliding braces H H H H, which can be raised or lowered by regulating screws. Attached to each of these wooden bars is a piece of canvas I, to give the slimes an even surface when the arms are rotating. The floor of the buddle is at K, and has a fall, varying with the nature of the work, from the circumference to within a certain distance of the central opening, where it becomes horizontal; L is the central annular opening for the escape of the "tailings," which pass away

by the launder M. N is the shaft, which, moved by any convenient power, gives motion to the washer—to the arms F F, and also the diagonal distributing launders O O O O.

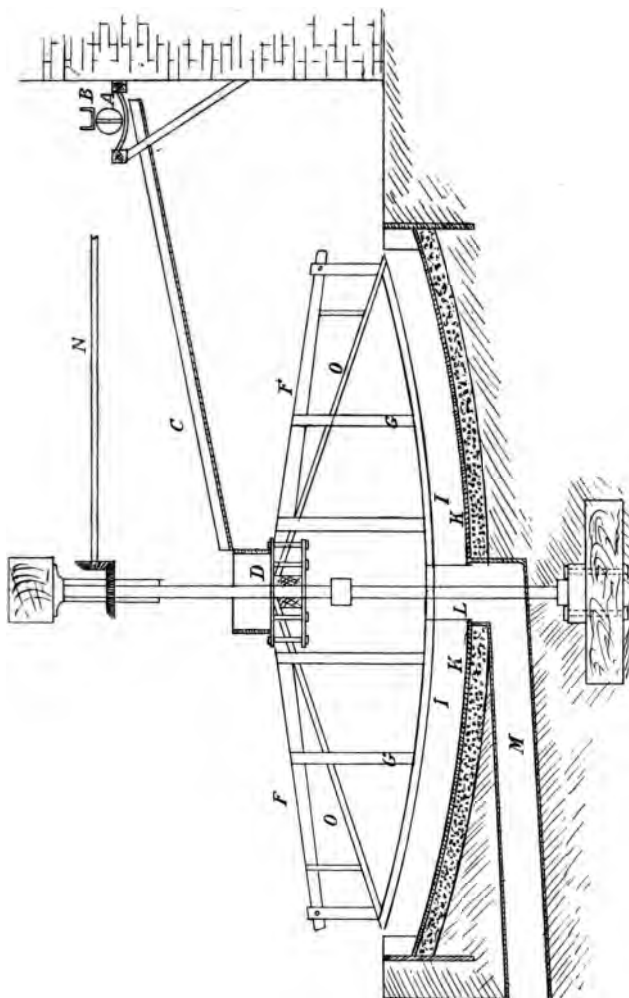


FIG. 1.—Hundt's Concave Circular Buddle.

These launders are in communication with the central trough D, from which, in their revolution, they carry the

slimes to and distribute them at the outer edge of the buddle. The speed at which the arms and distributing launders revolve vary with the nature of the slimes, from 8 to 16 revolutions per minute.

The syphon separator is another form of washing machine, and depends for its action on the upward flow of a current of water. According to Neve Foster, this machine is used largely at Metternich for the treatment of the soft, lead-bearing sandstones, and is capable of working up 270 to 300 cubic feet of crushed sandstone per hour. For a full description of the separator the reader is referred to that author's work on *Ore and Stone Mining*.

The jigging machine, or jigger as it is familiarly known, is largely used for washing lead ores; the simplest form, consisting solely of a sieve, containing the crushed ore which is moved rapidly up and down in a tub of water, the particles arranging themselves according to their density, the heaviest and richest portion being at the bottom.

An improvement on this simple form is seen in the jigger having the sieve stationary, the water being forced upwards through the crushed ore by the action of a piston working in a compartment below the sieve. The most efficient form of this washer is known as the "Hartz Continuous Jigging Machine," and described by the *Mining and Smelting Magazine* (1864). Fig. 2 represents a section of the jigger.

The work to be treated is shovelled into the inclined feeding hopper A in front of the machine, from whence it is gradually carried by the force of the stream of water from the launder P into the perforated trommel B. This trommel retains any obstructive matter, after which the pulp arrives at the jigging sieve C. In the bottom of this, a layer of coarse galena is placed from $\frac{1}{8}$ th to $\frac{1}{3}$ th of an inch in size, which acts to a certain extent as a filter, and, by checking the flow of the slime, enriches the ore before

the galena passes through the sieve. The fine rich ore, on

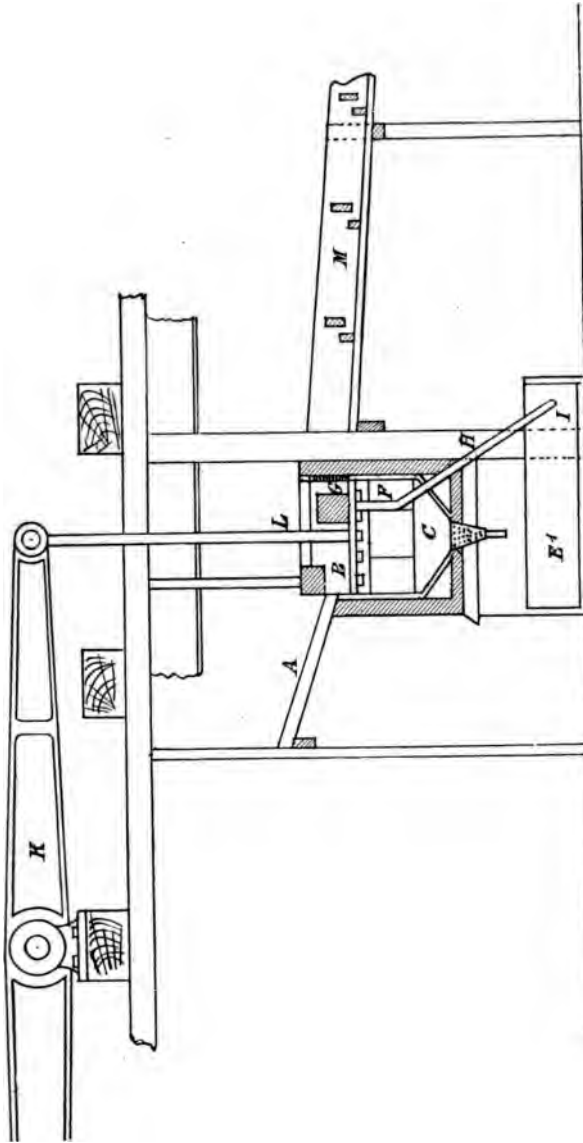


FIG. 2.—Hartz Continuous Jigger. Section.

leaving the sieve, falls into the conical hutch E, made of

zinc plates, and from thence into the bin E', when it is ready for the smelting house, making a produce containing 75 to 80 per cent. of lead if rich ores have been treated, or ready to be washed again on the buddle if very poor ores have been used. The larger grains of the ore that cannot pass through the sieve accumulate round the pipe F, which can be arranged to any required level, and is surrounded by a protecting cylinder G, to prevent the mixing of the grains. When these grains accumulate to the level of the pipe, they pass through it, by the zinc pipe H, into the bin I, placed beneath, and are then ready for smelting. The sieve has a slight inclination towards the cylinder G.

The apparatus is set in motion by the piston K connected with the rod L, and the number of strokes per minute is 140. In front of the apparatus is the launder M, furnished with ledges 2 feet long and 4 inches high, into which the lighter waste is carried by the stream of water forced up by the piston, through the openings placed on the top side of the hutch, from whence they pass to a flat buddle for further washing. By this machine, about 120 to 150 cubic feet of crushed ore can be dressed in a working shift of twelve hours by two workmen.

The shaking table or frame is another form of dressing machine used chiefly in the lead-mining districts of France, Belgium, and Germany, and is called in the two former countries "Table à Secousses," and in the latter "Stossheerde." In principle, it differs merely from the ordinary buddle in being subject to a shaking or percussion motion, which largely aids the separating process. For this purpose the frame is suspended by four chains, two at each end, those in front being attached to a roller, so as to allow the alteration of the inclination of the frame as required. The whole is supported by a framework of timber, and the

CHAPTER V.

SMELTING OF LEAD ORES.

IN the metallurgical processes for the extraction of lead from the dressed ores, the form of furnace depends on the nature of the ore treated: for instance, the smelting of galena is confined entirely to the reverberatory type of furnace; on the other hand, the native carbonate and sulphate of lead, or a mixed sulphide ore, is better suited for and is smelted in the shaft or blast furnace.

The systems in use may be classified as follows:—

1. Reverberatory furnace.
2. Open hearth.
3. Blast or shaft furnace.

In the first, the process is mainly an air-reduction one, by double decomposition; in the second, a deoxidisation by carbonaceous matter; and in the third, a deoxidisation and reduction by the aid of carbonaceous matter and iron oxide.

1. *Smelting in the Reverberatory Furnace.*

This type of furnace is well known in England as the Flintshire; it consists of two parts—one for the burning of the fuel, called the grate, and the other, the hearth or bed, on which the operation of smelting takes place, the separation being effected by a low ridge of brickwork termed the bridge, the whole being covered by a roof, having a declivity to one end of the furnace. The flame and products of combustion from the grate pass over the bridge, and,

(continues the author), these conditions are not brought into effect in the majority of electro-magnetic separators. Very narrow fields are awkward for separation, and, on the other hand, crushing the ore to uniform grains is not easily accomplished.

Theoretically, the diameter of the grain need not exceed the width of the field, but in practice twice the distance is required. Direct contact of the particles of ore with the bare poles is hardly feasible, owing to the manner in which the ore has to be conveyed; as the material is attracted with variable intensity by the two poles, actual experiments must decide the exact distance at which it must be passed.

The magnetic separators, of which various forms are in use, are worked with endless canvas bands, with rolls, or by deflection with fixed magnets. The Conkling machine is a good representative of the endless belt system of working. It consists (*English Mining Journal*, vol. liii., 1892) of two iron rollers, round which travel, at a certain inclination, a canvas band, 3 feet broad. Between the upper and lower layers of canvas is fixed a series of electro-magnets. The feed is from a hopper placed directly over the lower roller, and as the crushed ore falls on the band it is carried over the magnetic field, receiving, during the passage, a washing from a current of water. The magnetic particles adhering to the band are carried over the higher roller, while the non-magnetic portion of the ore is washed away at the lower.

In the roller system of separators (*English Mining Journal*, 1883) the crushed ore is allowed to drop between revolving rollers, supported on, or containing within, electro-magnets. The non-magnetic particles fall through unaffected by the magnets, while the magnetic portion is attracted by and adheres to the rollers, falling off at a point in their

internal lining of good refractory material to resist the dissolving action of the lead, the structure being well tied together

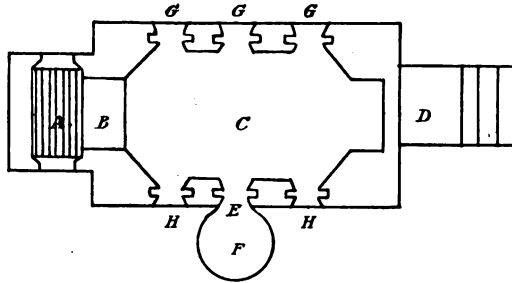


FIG. 4.—Plan.

with tie-rods. The dimensions vary in different works: the following, however, is a general internal measurement—

	Feet.	Inches.
Length of fire-place	2	3
Width "	4	0
Length of hearth	10	0
Width " (middle)	9	0
" " (flue end)	8	3
Top of bridge to roof	1	6
Height of doors	0	8
Width "	1	0

The hearth of the furnace is formed by the slag taken from a previous smelting, which is softened to a pasty mass and then rabbled evenly over the surface; this is repeated until a depth of 7 to 8 inches is obtained. The decline of the hearth is to the working side, and forms a well 16 inches below the middle door, and into this cavity runs the metal produced during the operations in the furnace. In the section and plan, the different parts of the furnace are marked as follows:—

- | | |
|--------------------------------|-----------------------------|
| A. Fire-grate. | B. Fire-bridge. |
| C. Hearth. | D. Flue. |
| E. Tap-hole. | F. Lead-pot. |
| G G G. Doors, labourers' side. | H H H. Doors, working side. |
| I. Hopper. | J. Charging door for fuel. |
| K. Well. | |

After running off the metal and slag from the previous smelting, the furnace is partially cooled by opening the doors and lowering the dampers, the hearth meanwhile being evenly spread and made ready for the next charge. This cooling down to a very dull red heat is necessary, otherwise the charge of galena would melt, and roasting would become impossible.

The weight of the charge varies in different localities; in some it is only 12 to 14 cwt., while others rise 20 to 25 cwt.; generally, however, a charge of 20 cwt. is used.

The furnace being ready, the charge of ore is dropped through the hopper I, and then spread evenly on the upper parts of the hearth C, care being taken to keep the lower part, or the well, K, clear. With the closing of the doors, and the checking of the draught, by suitably lowering the dampers, commences the first stage of the operation, technically known as the first fire, and resulting in the partial oxidation of the sulphide to oxide and sulphate of lead with evolution of sulphurous acid gas. During this stage, little or no fresh fuel is used, the low fire in the grate, along with the heat retained by the furnace from the working of the previous charge, being sufficient to effect the necessary chemical changes. From time to time, the ore is turned over from the labourers' side of the furnace with a rabble, to expose fresh portions to the unconsumed oxygen which passes over the hearth. At the end of an hour and a half, the white fumes, given off copiously during the operation, are seen to diminish considerably in quantity, and the furnace doors are opened for a short time to furnish additional oxygen to complete the proportions of oxide and sulphate necessary to react on the unaltered sulphide in the next stage. In two hours from the start, the first roasting has been carried far enough.

Fresh fuel is now added to the fire, the furnace doors are

closed, accompanied with a raising of the dampers, the heat being increased to bright redness, and the second stage is entered on. During this stage a large reduction to the metal is effected, the lead running down the slope of the hearth to the well K. After an hour's exposure to this temperature, the doors on the working side are opened, to cool the furnace a little, a result which materially aids the reduction and separation of the metal. Meanwhile the slags, which have become pasty and with a tendency to run, are stiffened with a little quicklime thrown over them, which, after mixing, are thrust back with the rabble on to the higher parts of the hearth. The quicklime acts both mechanically and chemically. The mechanical part, in addition to rendering the slags more workable, and thus effecting a better separation of the lead, also assists the action between the oxide and sulphide, by lowering the fusibility of the mass; while, chemically, any silicate of lead formed during the operation, is broken up by its use, liberating the oxide of lead, so that it may react on any unchanged sulphide present.

The doors are now shut, and the third stage commenced by throwing on the grate more fuel to bring the heat to bright redness. This is continued for an hour, and the working doors again thrown open, and the pasty slags, stiffened by the addition of more quicklime, are thrust back from the lower parts of the hearth, which now contain a large proportion of metallic lead.

In the fourth and last stage of the smelting, the doors are closed, and the heat again raised to bright redness for an hour. The tap-hole is now pierced, and the molten lead allowed to flow into the lead-pot F, placed adjacent to the middle door. The slags are again stiffened with a little quicklime, and raked out through the doors on the labourers' side of the furnace, to be afterwards smelted, for the lead

they contain, in the slag-hearth. The time occupied in working a charge of 20 cwt. of ore is about five hours, and the coal consumed averages 13 cwt.

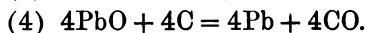
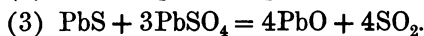
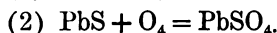
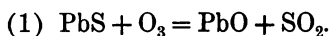
The surface of the molten metal in the pot rapidly oxidises, forming a rich dross, which is skimmed off and returned to the furnace. Meanwhile, preparations are made to run the contents into moulds to form what is technically known as "pig lead." In this state the metal is "hard," and quite unsuitable for industrial purposes, containing, as it does, such impurities as iron, zinc, antimony, and also the whole of the silver originally existing in the ore, as sulphide. The silver, a very important item to the smelter, is removed by either the Pattison or Parkes desilverization method, and the lead is "softened"; that is, the impurities are removed by oxidation in the calcining furnace, to be described hereafter. The slag produced amounts to 20 to 25 per cent. of the weight of ore treated, and contains a high percentage of lead as oxide and sulphate. The following analyses represent the composition of slag, from the Flintshire reverberatory furnace:—

	(1)	(2)
Silica	20.95	17.47
Fluoride of calcium
Sulphate of barium	2.48	...
Protoxide of iron	3.59	2.42
Oxide of zinc	12.16	18.17
Lime	21.37	28.04
Sulphide of lead	6.14	1.25
Sulphate of lead	20.05	26.88
Oxide of lead	12.13	5.77
Metallic lead	1.05	...
Carbon	Trace	...
	<hr/> 99.92	<hr/> 100.00

French Process of Reverberatory Smelting.—The reactions, on which rest the working of the reverberatory furnace in

France, differ somewhat from those of the English, the main object of the roasting being to form a large proportion of sulphate of lead along with a small portion only of protoxide of lead, the former ultimately acting on the unaltered sulphide, at a higher temperature, forming protoxide of lead and sulphurous acid, the reduction of the protoxide to the metal being effected at a later stage by carbonaceous matter.

The following equations represent the reactions occurring during the process:—



Any unacted sulphate left in the charge is reduced by the carbon to sulphide, and then, by reaction with another portion of sulphate, forms protoxide of lead by equation No. 3, which is ultimately converted into metallic lead by equation No. 4.

The structure of the furnace varies but little from the Flintshire type, the difference being that the doors (three in number) are placed in the front or working side of the furnace.

Fig. 5 represents a section of the French reverberatory furnace.

- | | |
|-----------------------|----------------------------|
| A. Fire-grate. | B. Fire-bridge. |
| C. Hearth. | D. Flue. |
| E. Tap-hole. | F. Lead-pot. |
| G G G. Working doors. | H. Hopper. |
| I. Well. | J. Charging door for fuel. |

In working the furnace, the charge of 20 cwt. is run through the hopper on to the hearth, and evenly spread on its uppermost parts. The temperature is low at the commencement, but as the action proceeds it is gradually raised

to a point approaching dull redness. At the end of two hours, a thick white crust of sulphate of lead is found to

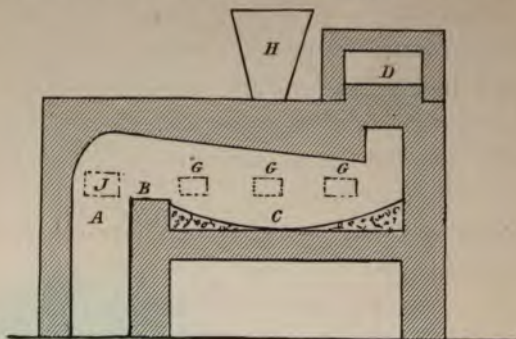


FIG. 5.—French Reverberatory Furnace. Section.

have formed on the surface of the charge. The doors are now opened, and the mass is vigorously rabbled to produce an intimate mixture of the whole. On closing, and raising the temperature, the sulphate reacts on the unchanged galena, and yielding, after two hours' exposure, a large proportion of litharge or yellow oxide. The final stage is the reduction of this product to the metal; and for this purpose, the doors are again opened, and the furnaceman throws into the furnace several shovelful of small coal, intimately mixing it with the mass on the hearth. After clearing the well for the reception of the lead, the doors are closed, and a brisk fire is made up on the fire-grate. The lead now begins to trickle down the sloping hearth, and as the temperature increases, the greater becomes the reduction, the well being gradually filled with the molten metal, which is tapped off into the lead-pot. A further addition of small coal is made to the pasty slags, the temperature again raised, which reduces to the metal the remaining portion of the protoxide, along with any unacted sulphate of lead. The metal is cast into "pigs," and then desilverized and refined in a manner similar to the English procedure.

Austrian Process of Reverberatory Smelting.—At Raibl and Bleiberg in the province of Carinthia, the ore is well adapted for reverberatory smelting, being mined from the beds of the Alpine limestone, and containing a good percentage of the metal.

The process is based on chemical reactions similar to those taking place in the French furnace, and, in working, the yield, as stated by Thum, is 60 to 65 per cent. of the metal, the lead in the ore being 65 to 70 per cent. This shows a loss of 5 per cent., of which perhaps half is found in the residues of the furnace. They are collected, washed, and treated with the furnace slags.

Figs. 6 and 7 show the elevation and plan respectively.

In construction, two furnaces are built side by side and

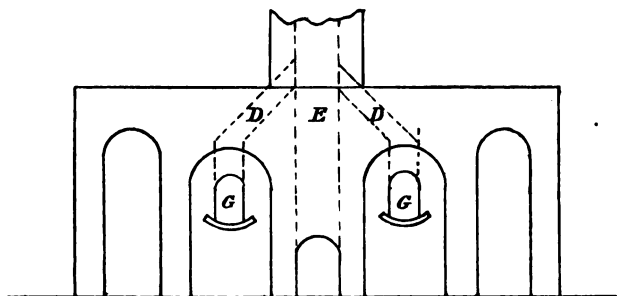


FIG. 6.—Bleiberg Furnace. Elevation.

work into one chimney. Thum, in describing the Bleiberg furnace, says it is 10 ft. 4 in. long and 4 ft. 10 in. wide, and the fire-bridge is 4 ft. 2 in. long by $5\frac{1}{2}$ in. broad, with a flue 9 in. wide. As will be seen from the drawings, the sole of the bed has an inclination of $9\frac{1}{2}^{\circ}$ towards the working door G, at the narrow end of the furnace. The fire-door is situated at the same end of the furnace, and opens to the fire-place, which is constructed alongside of and in the direction of the length of the bed and with the same inclination. The opening to the flue D is just in front of

the working door, and communicates with the flue passing over the two furnaces leading ultimately to the common

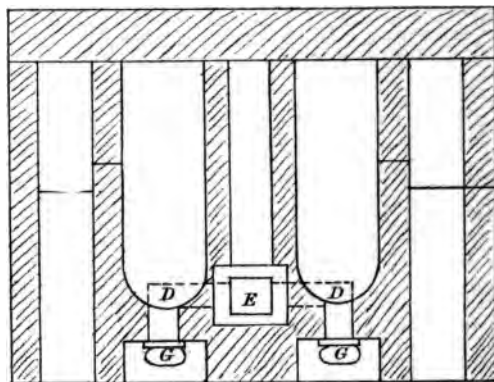


FIG. 7.—Plan.

chimney. At the working door G, a cast-iron plate is fixed, hollowed out in the middle, which enables the lead to flow direct into the mould placed beneath. The furnace is constructed with ordinary fire-brick and slabs of bunter sandstone; the latter material, although containing a considerable amount of iron, is considered sufficiently fire-proof for the interior parts. Only the sole of the hearth is made of refractory clay, which is rounded at the sides, and thus enables, with its inclination, the metal to flow off from all sides of the working floor. In order to avoid any considerable loss of lead from the fissuring of the sole, it must, after being laid down, be perfectly air-dried, and then subjected to a gradually increasing temperature; afterwards the smelting of the slags forms a compact impervious glaze, which prevents any absorption of the lead. The sole requires to be renewed every four to five weeks.

The practical working of the furnace consists of three stages—roasting, stirring, and pressing; and the charge of ore averages $3\frac{1}{2}$ cwt. Before charging, the furnace is allowed

to cool to a dull red heat, and the charge is then thrown through the working door and evenly spread on the higher parts of the hearth. The retained heat, assisted by a little fuel thrown on to the low fire in the grate, soon ignites the sulphur of the ore, and the first or roasting stage, commences. For three hours a low red heat is kept up, and the charge is moderately stirred from time to time. When the sulphurous fumes disappear and the lead is seen trickling down to the front of the furnace, the temperature is raised considerably, and the charge stirred every quarter of an hour, so that the various portions may be brought to react on each other at an equally high temperature. In five to six hours, the "stirring" process is done, and the furnace is cooled down to some extent to enable the workman to gather the charge into a heap; this done, he covers it with several shovelful of burning fuel from the grate, and intimately mixes the whole together. The temperature of the furnace is raised as high as possible, and the third or "pressing" stage commences. This consists principally of working the charge well up together at the highest possible temperature, at the same time repeating the addition of carbonaceous matter, until, within about three hours, the remainder of the lead runs off through the working door. The slags, rich in lead, are washed and re-smelted as before mentioned.

2. Smelting in the Scotch or American Ore-Hearth.

Smelting in the ore-hearth yields a purer lead than what is obtained from the reverberatory furnace. The hearth also costs much less for construction, and the outlay for fuel and labour in working is lower.

The rudest type of the ore-hearth is the primitive form known as the Backwoods hearth, which consisted of a square chamber built in such a position as to be exposed to the prevailing wind. In the chamber were placed layers of

thrown on, some lime also being added to check the fusibility of the silicates. Reduction to the metal now commenced, the lead trickling down through the interstices of the fuel to the bottom of the hearth. This withdrawal of the "brouse" from the furnace, and the building up anew of the fire, along with frequent stirring of the mass to prevent vitrefaction, was carried out at intervals of half an hour, during a twelve hours' working of the furnace, and by this time a considerable portion of the lead had been reduced, and was discharged by a gutter to a "sump" or outer basin, from whence it was cast into "pig" moulds.

The waste arising from the volatilisation of lead and its poisonous effects on the workmen, led to the modern type of

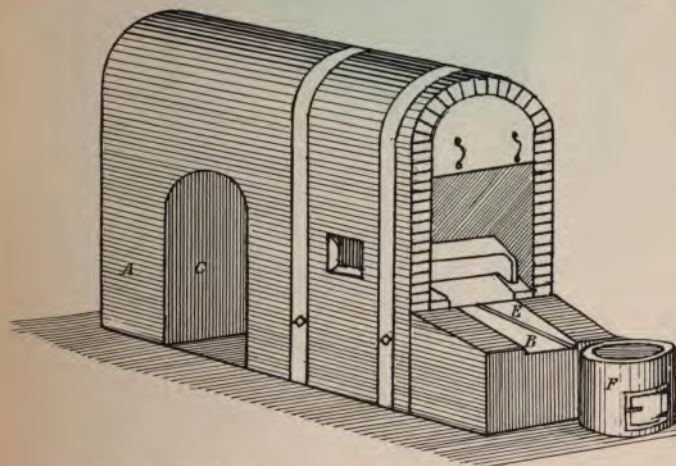


FIG. 9.—Enclosed Ore-Hearth Furnace. Elevation.

the hearth furnace now used in this country. In Fig. 9 it is shown arched over the top, and connected with a flue A to convey the "fume" to a suitable condensing arrangement for recovery. The sides and bottom of the hearth are lined with cast-iron plates, and in front is placed the sloping iron plate B forming the work-stone. In the opening C

access is obtained to the tuyeres placed at the back of the hearth, which is charged with ore and fuel through the aperture D. The lead on reduction runs from the hearth by a gutter E to the melting pot F, heated by a separate fire, and then moulded into "pigs" for further treatment. The working of the "enclosed" is similar to that of the "open" hearth, already described.

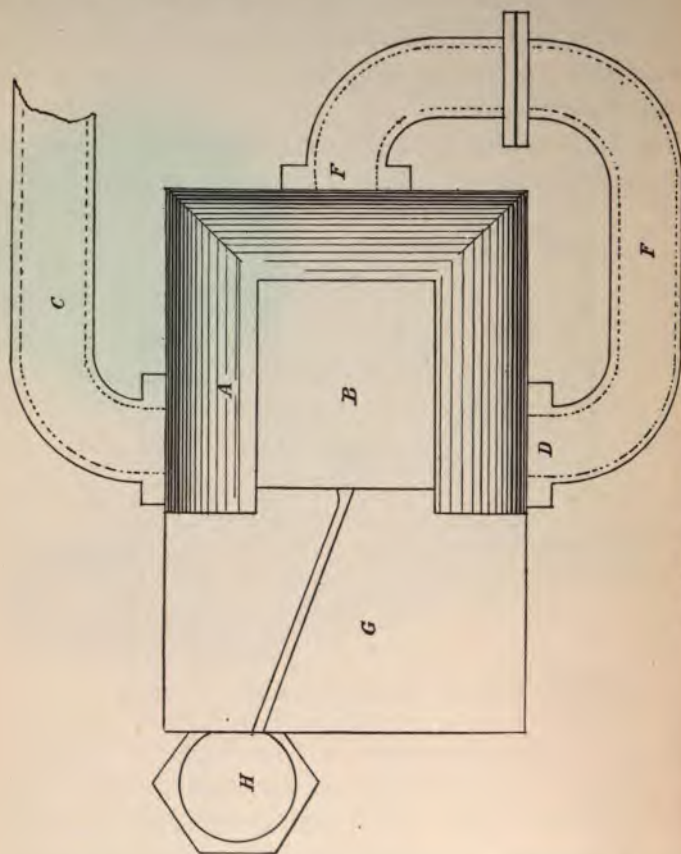


FIG. 10.—American Ore-Hearth. Plan.

The furnace known as the American ore-hearth is a considerable improvement over the Scotch type, inasmuch as

rom its construction, the air before entering as blast through the tuyere is heated up to 150° C., by circulating round the hearth, and thus effects a better reduction, in addition to saving fully 10 per cent. of fuel during each shift. In Fig. 10, A represents the casing or jacket made of cast-iron and fixed in the upper part of the hearth B. The cold air is forced into the casing through the pipe C, and emerges at D, passing from thence in its heated state to the tuyere E by the pipe F. The work-stone G is also made of cast-iron, with a gutter for the melted lead to flow into the pot H. Practically, the working conditions are the same as those of the "enclosed" hearth, and the yield of metal averages 80 cwt. in a double shift of twenty-four hours.

The successful working of the ore-hearth, necessitates a carefully regulated and divided blast to produce just sufficient heat to effect the reduction of the ore without fusing the contents of the hearth into a slag. During the working, the mass of "brouse" requires constant stirring, otherwise it would become a vitrified body, through which the heat could not penetrate, nor could any reduced lead find a passage through it to the bottom of the hearth. The lime plays no chemical part in the reduction of the "brouse," but is only added to correct any tendency of it to become pasty, which may arise from the nature of the ore, or to excessive heat of the hearth. Its use should therefore be limited to this mechanical action.

The ore-hearth makes a division of the ore into lead and a vitrified product known as grey-slag. Some rich slags and hearth-ends, containing partially reduced "brouse," are also produced, and are treated afresh in the ore-hearth. The accumulation of grey-slag, whether from the reverberatory or ore-hearth furnace, is worked up in the slag-hearth yielding lead and black-slag.

The following analysis represents the composition of ore-hearth slag:—

Oxide of lead	22.68
Sulphate of lead	17.22
Sulphide of lead	3.39
Metallic lead	2.82
Oxide of iron	6.19
Oxide of zinc	12.35
Fluoride of calcium	2.76
Sulphate of barium	3.02
Lime	18.64
Alumina	2.02
Silica	8.78
	<hr/>
	99.87

Smelting of Grey-Slags.—The grey-slugs produced by reverberatory and ore-hearth furnaces, are treated in slag-hearth for recovery of the lead they contain. operation of smelting in this hearth, differs from that of ore-hearth in this, that in the latter the ore to be operated on does not undergo an entire liquefaction or fusion of parts, but only a partial one at a moderate heat, whereas the slag-hearth the contents suffer a total dissolution at a high temperature. The slag-hearth also differs from other in its construction and in the materials of which formed, the sides being built of fire-brick or refractory stone to resist the intense heat. Figs. 11 and 12 represent the sectional elevation and plan of a slag-hearth. dimensions are 26 in. in length from the back to the stones, by 20 in. in width and 33 in. in depth, in measurement. A is the body, B the tuyere, C an iron plate forming the bottom of the furnace, D an earthen pot for receiving the slag and metal from the hearth, E a slag tank, and F is a lead-pot for receiving the metal from the outer pot D. The iron plate C, and the outer pot

are covered with a thick layer of coal ashes, tightly rammed down, which forms a filter to separate the lead from the slag.

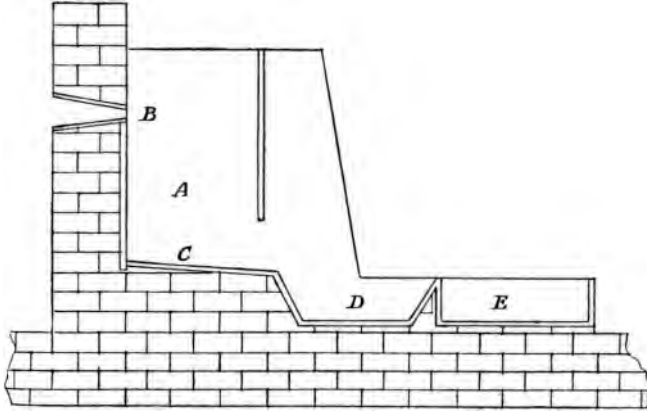


FIG. 11.—Slag-Hearth. Section.

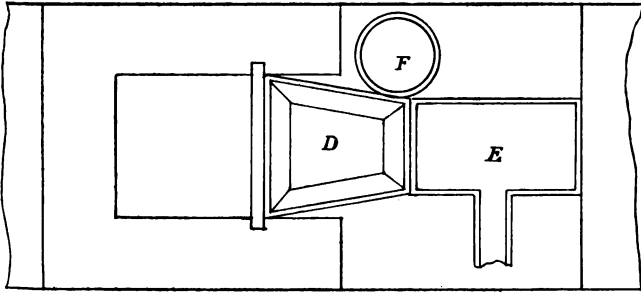


FIG. 12.—Plan.

Lead is too heavy, and, when in fusion, too subtle a body, to float upon coal ashes; slag, on the other hand, is too light, and at the same time too thick a substance, though in fusion, to sink in such ashes; consequently, when two such substances are distinct (and passing through the high temperature of a slag-hearth makes them so) and when they are deposited on the layer of ashes, the heavier lead will sink through, while the lighter slag will float on the surface. This bed of coal ashes is also of further use in conveying from the hearth to

the outer pot D of the slag upon, and of the lead beneath its surface. From this outer pot, the molten metal is conveyed through an opening in the bottom to the lead-pot F, and thence cast into pig lead. The slag meanwhile floats over the layer of ashes in the pot D, and is discharged into the tank E, containing water. Being porous in its nature, the slag still retains some minute particles of metallic lead in its pores, and on this account it is generally re-smelted in the slag-hearth after washing. The shift lasts about twelve hours, and the charge of reverberatory and ore-hearth slags, black and litharge slags, lead clay-hearths, and coal cinders, along with coke as a fuel, is fed into the furnace at intervals. The well-doing of the shift largely depends on the formation of a "nose" to the tuyere, which is a protuberance of coagulated slag gathered round the nozzle, and which, if in right form, enables the stream of air to be carried to the centre of the hearth, and so divided into channels that it equally spreads through the mass.

Richardson's Slag-Hearth.—Around Newcastle is used a form of slag-hearth devised by Richardson. It is circular in form, with a height of $8\frac{1}{2}$ ft. and $2\frac{1}{2}$ ft. diameter, and is built of fire-bricks. The bed, consisting of tightly rammed clay and coke-dust, is depressed in the centre to allow the reduced lead to collect, and the blast is provided by three tuyeres. The charge enters the furnace at the top, and the molten lead and black-slag are discharged from the bottom by suitable channels.

Spanish Slag-Hearth.—This form of furnace has been found very economical in working, and is much used in the smelting of grey-slags. In Fig. 13 a section is shown.

It consists of an upper chamber A resting on four cast-iron columns, B B in section, while C is the lower part or body of the furnace, which can be renewed when necessary without disturbing the upper chamber. The bed D is made of clay and

coke-dust tightly rammed in, and is saucer-shaped to allow the metal to collect, and which is run off at intervals into

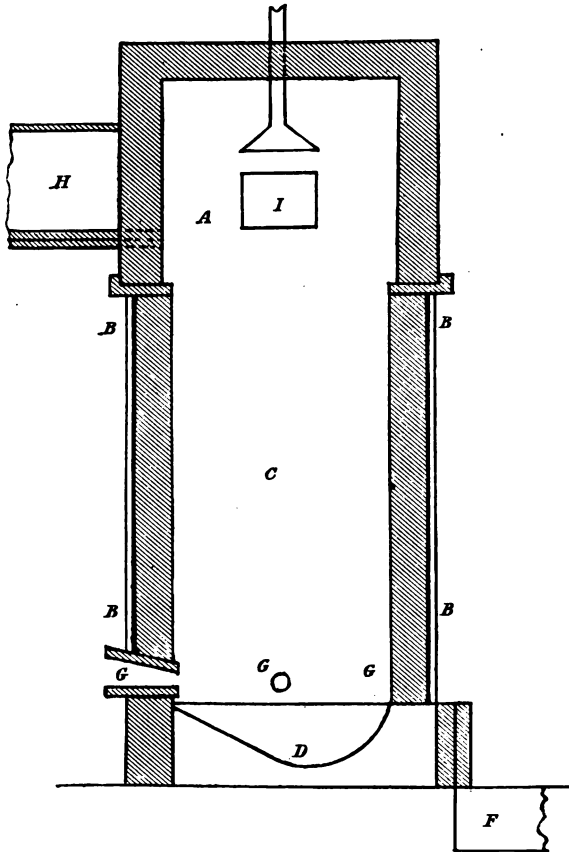


FIG. 13.—Spanish Slag-Hearth. Section.

the pot E. The black-slag formed flows from an opening in the breast of the furnace to the tank F, containing water. In the body, three tuyeres, G G in section, are provided to admit the blast, and the charge of slag, fuel, and flux, generally fluor-spar, is thrown in through the door H, and the fumes pass off at I into condensers.

Chemically, the action going on in the slag-hearth is the formation of a black-slag by the union of the silica and alumina in the clay, with the lime, oxide of iron, and other ingredients of the grey-slugs used. The coke acts as a reducing agent on the oxide of lead, yielding metallic lead of a very inferior quality.

3. *Smelting in the Shaft or Blast Furnace.*

In many localities on the Continent, and also in Australia and America, mixed ores are found containing galena, with sulphides of iron, copper, zinc, antimony, silver, etc., and, from their complex nature, are found unsuitable for treatment either in the reverberatory or the ore-hearth furnace. Consequently, the shaft or blast furnace is used for their reduction. The Silesian furnace is of this character but the more modern types are known as the Piltz and the Raschette furnaces. Among American smelters, the latter finds favour, while the former has a wide use in Germany, Austria, and other countries.

Silesian Furnace.—In Fig. 14 a section of this class of furnace is seen. It is built of common red bricks A A with an inner lining of fire-bricks B B. From the mixing floor downward, the furnace is rectangular; above the floor, it is circular in form. The charging door D is on a level with the mixing floor, from which the mixture of ore and flux is thrown into the furnace. A little above the dished bed of the blast F enters, and the slag produced during the working is floated off at G. A channel H leading from the bottom of the bed of the furnace, which previous to the charge is plugged with clay, carries to an outside lead-pot the reduced metal. At the upper end of the furnace is placed the exit I in communication with a flue for carrying away the fumes. In charging, a mixture of 100 parts ore and 25 parts iron slag (ferrous silicate) is used, and the

fuel consumed (coke) constitutes an equal weight of the charge.

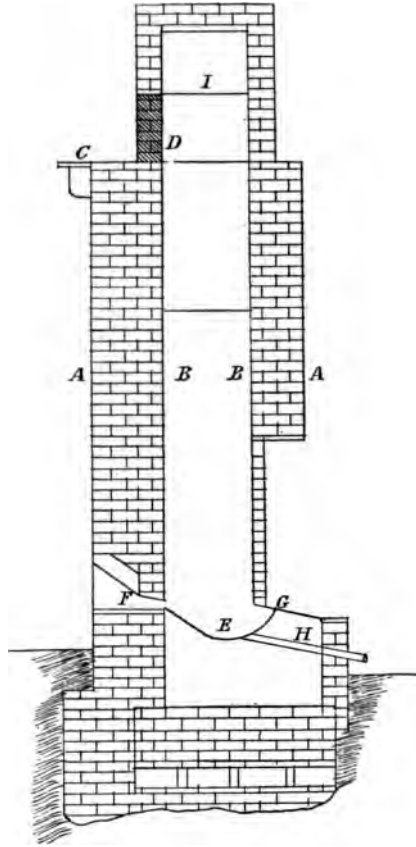


FIG. 14.—Silesian Blast Furnace. Section.

Piltz Furnace.—Fig. 15 is a section of this type of furnace. It is built in two sizes—a large and a small Piltz. The former is worked with eight tuyeres, and has a charging capacity of 40 tons, while the latter has only four, and is limited to a 20-ton charge. The furnace is built of fire-bricks enclosed in an iron casing, and tapers from a diameter of 7 ft. (large Piltz) at the charging platform A, to 5 ft.

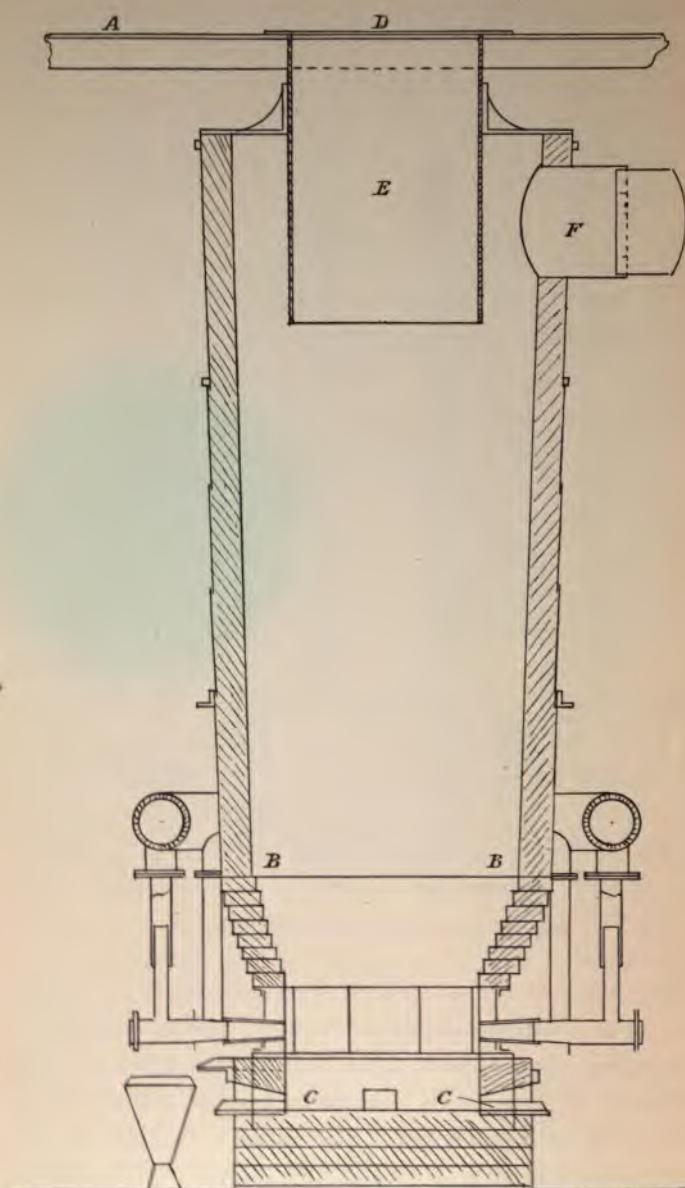


FIG. 15.—Piltz Furnace. Section.

at the tuyere zone B, which is encircled with a series of cast-iron chambers, forming a jacket, through which flows a current of water to prevent over-heating at this, the hottest part of the furnace. Underneath is the hearth C, some $2\frac{1}{2}$ ft. thick, and built up of layers of fire-bricks resting on an iron plate. On a level with the hearth are placed the four tapping-holes, equidistant from each other, and, at a point below the tuyeres, two openings are left for running off the slag. The ore and fuel is charged from the top D, being shot down through an inner tube E, $4\frac{1}{2}$ ft. in diameter, and the outlet for the products of combustion and fume is at F, the exit pipe being placed above the end of the charging tube, and thus allows a clear passage for the gases.

A charge of 40 tons of a mixture of medium and poor complex ores will yield about 63 cwt. of silver-lead, along with a regulus of copper, iron, etc., weighing 15 cwt.

Raschette Furnace.—The Raschette type is rectangular in form, and the cost of construction is less than the Piltz. It is built of fire-bricks, and tightly clamped with tie-rods. The height varies, in some districts being 20 ft., with a length of 8 ft. and a width of 4 ft. The lower part of the furnace is jacketed as in the Piltz, and the reduced lead is "syphoned off" by means of a channel connecting with the hearth at one end, and at the other a lead-pot placed adjacent to the furnace. In providing the blast, six tuyeres on each side are generally used, having a pressure of 2 lb. on the square inch. The charge of ore and fuel varies from 20 to 35 tons, according to the capacity of the furnace.

Roasting.—Lead ores are generally roasted or calcined before smelting in the blast furnace. The calcination was formerly carried on in the open air, the ore being built up in the form of a pyramid on a thick layer of pine wood, and then covered with fine roasted ore from a previous burning, the covering preventing any injurious action by the access of

an excess of air. As the combustion proceeded, it was supported by the sulphur of the sulphides, and the calcination of a charge of 100 tons lasted from two to three months.

The modern method of roasting is carried on by the reverberatory furnace, and for this purpose it is built some 50 ft. long, with a hearth and fire-place 10 ft. wide. The ore is fed in at one end, and gradually worked up to the bridge, whence it is withdrawn in a clotted form, allowed to cool, and then broken up to a size suitable for smelting in the blast furnace. By the roasting action, a portion of the sulphur is eliminated as sulphurous acid gas, in addition to the formation of oxides and sulphates, while the roasted mass still retains 6 to 7 per cent. of sulphur, as sulphides—a necessary precaution for the after separation of any copper present.

Chemical Changes occurring in the Blast Furnace.—In the blast furnace the reaction is mainly a reducing one, through the action of incandescent fuel (carbon) and carbonic oxide, this gas being generated in front of the tuyeres by the action of the blast on the carbon, the union with the oxygen supplying the necessary heat to melt the slag and metal. The lead chiefly existing as oxide on descending the furnace comes into contact with the gaseous carbonic oxide and fuel, and is quickly reduced to the metallic state, along with the silver contained in the original charge. The sulphate of lead present, becomes reduced to sulphide, and combines with the variable proportions of copper, zinc, iron, etc., existing in the roasted ore, forming the second product known as “regulus”; while the silicious matters form silicates with any unreduced oxides of a more or less fusible nature, which runs from the furnace as slag.

The accretions often found hanging to the inner lining of the blast furnace, and which cause much trouble in the

working of the furnace, is due mainly to the accumulation of particles of zinc sulphide, intermixed with varying proportions of silica, iron, manganese, lime, and copper. In dealing with this obstruction, Mr. M. W. Iles (*School of Mines Quarterly*, November 1896) advocates the disuse of scrap iron with ores heavily charged with zinc, since heated metallic iron decomposes zinc sulphide. He further recommends taking the gases from the centre instead of from the back-end wall of the furnace, and suggests a more uniform distribution of the ore-fluxes and fuel over the entire top, which cause the furnace to drive faster, and thus lessen the tendency towards "hangings."

Some recent Improvements in the Treatment of Complex Ores.
—According to the *Queensland Government Mining Journal*, January 1900, a new process has been introduced with success for the calcination of ores containing galena. The ore is mixed according to the proportion of sulphur present with from 6 to 15 per cent. of lime, heated in a reverberatory furnace to about 700° C. and then cooled down to 550° C., with the result that from 25 to 30 per cent. of lead sulphate and 2 per cent. lead oxide are formed, without the separation of any metallic lead. The amount of sulphate produced is proportional to the oxygen in the lime present, which, however, is not altered by the reaction, and apparently serves only as a carrier of the atmospheric oxygen. The operation is continued until 5 per cent. of unchanged sulphide of lead remains, when the product is withdrawn from the furnace, pulverised, transferred to a converter, and subjected to an air-blast at a pressure of about 1 inch of mercury. In a few moments a notable rise of temperature is observed from the oxidisation of the residual sulphide and the joint action of the sulphate and air. The mass becomes pasty, and evolves dense fumes of sulphurous acid gas, and finally solidifies when the operation is finished. The product is essen-

tially a mixture of lead oxide with sulphate of lime, and, if the ore is silicious, lead silicate, the sulphur being entirely removed even when other sulphides are present. Finally, the reduction to metal is carried on in the blast furnace.

The process is said to work well, with a saving of nearly half the fuel formerly used, with diminished losses of lead and silver and greatly reduced cost for labour. About 38,000 tons of ore are treated annually by this method, the whole of which is reduced in a single water-jacketed blast furnace.

Kirkpatrick-Picard (1900) in his treatment of complex sulphide ores containing lead, zinc, gold, silver, sulphur, etc. (the type of the well-known Broken Hill sulphide ores), proceeds as follows:—The ore is ground in a suitable mill, and then submitted to an oxidising roast in a reverberatory furnace, with the object of producing the maximum amount of oxides of lead and zinc and the minimum amount of sulphates. The sulphurous gases produced during the roast are collected and utilised. Inasmuch as it is impossible in ordinary roasting practice to convert all the lead sulphide into oxide, means are taken to keep at the lowest point the amount of lead sulphate produced. With this object, after the first stage of roasting is finished, and in order to get the ore as far as possible into the form of oxides, a small quantity of small coal is added to the partially roasted mass while still in the furnace. When finished, the roasted ore is withdrawn and mixed with powdered coking coal as a reducing agent, and in order that in the subsequent treatment the mixture of coal and ore may coke into coherent masses. The mixture is now submitted to a zinc-distilling temperature in a retort or muffle furnace, in such a way that the flames or gases from the furnace shall not come direct in contact with the ore charge. The result is the production of metallic lead and zinc. At the temperature of the furnace the zinc is

volatilised and condensed in the usual way, and the lead, gold, silver, iron, and silica are left in the retort, suspended or hung up in the carbonaceous sponge formed by the coke, to be subsequently smelted.

In order to prevent the deleterious effects of the lead upon the retorts, the coal used is of a bituminous character.

The residue, after the extraction of the zinc, is smelted in the blast furnace for the recovery of the lead, gold, and silver, and separation therefrom of the iron and silica.

A very interesting process, depending on the difference between the volatilising points of lead and zinc oxide, has been invented by Pape and Witter (1900). The idea consists of roasting the mixed ores so that one part of the metallic oxides produced, is caused to pass away simultaneously with the furnace gases from the roasting chamber, while the other is directly precipitated in the chamber. Fig. 16 is a section of the furnace used. To carry the process out, finely powdered sulphide ores are fed from a hopper A in a thin stream into the combustion chamber B, the walls of which have been previously heated to a high degree, and into which heated air currents from the flue C are introduced. By this means the ore is oxidised instantaneously as it falls on to the hearth of the furnace. If the ore contains sufficient sulphur to support combustion, no further addition of fuel is necessary during the working; if not, fresh charges of fuel are necessary to keep up the temperature of the chamber. While the non-metallic constituents of the ore fall, together with the greater part of the oxides of lead, silver, iron, and copper, on to the bed of the furnace, the greater part of the zinc oxide, along with a small proportion of lead and silver oxides, will escape with the furnace gases at the exit D, passing thence into cooling chambers or condensers, for the recovery of the metallic oxides.

In the zone marked 1, sulphurous acid is formed, and oxides of the non-volatile metals which fall on the sloping

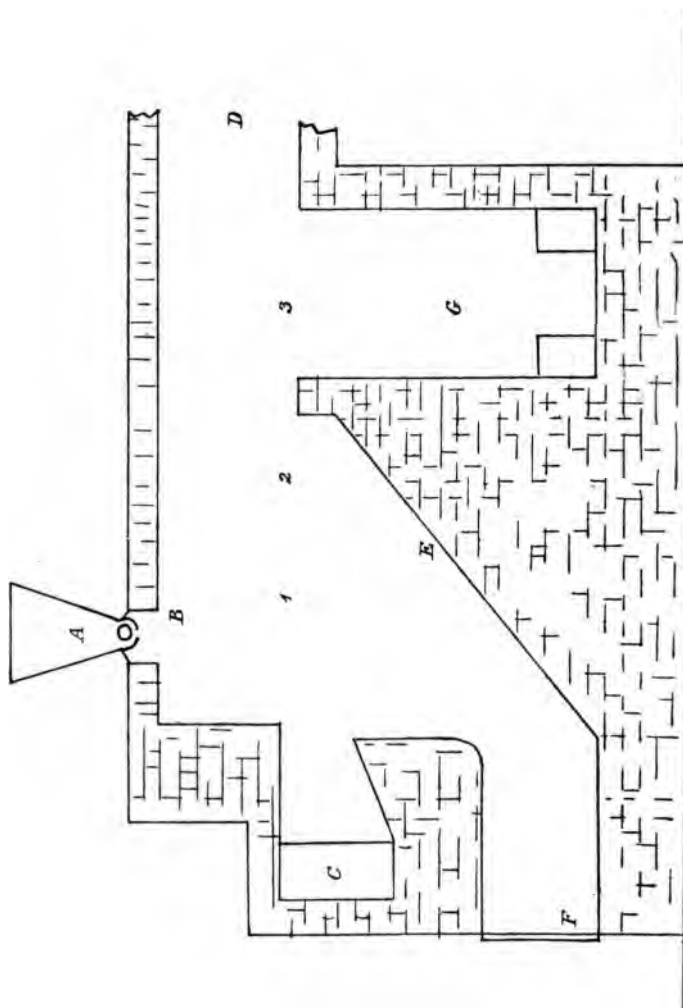


FIG. 16.—Roasting Furnace. Section.

floor E, and are removed for reduction through the door F. In zone 2, the volatile metals separated from the sulphur exist in a state of vapour, and become oxidised

in zone 3, some of the oxides falling into the division G, while some pass through with the fumes at the exit D. The collected oxides and the condensed fume are treated in the blast furnace for reduction to the metallic state.

At Ellesmere Port, the Smelting Corporation Limited carry on an ingenious method for treating mixed ores, which is described fully by Mr. Julius Vogel, their consulting chemist, in the columns of the *Engineering and Mining Journal*, New York (1900). The works are designed to smelt 90,000 tons of ore per annum, and all the motive power is supplied by electricity supplied from two continuous-current multipolar generators, each of 400 kilowatts capacity.

The ore, after unloading, is first crushed to $\frac{3}{16}$ in. in size, and then wheeled to the calciners, which are of the revolving-table type, and each capable of treating 12 to 15 tons ore every twenty-four hours. After calcination, the wasted mass is pressed in briquettes, 4 in. diameter and $2\frac{1}{2}$ in. deep, and then smelted in a water-jacketed type of blast furnace, fitted with a "syphon" arrangement, to run off the lead without interfering with the working of the furnace. The fluxes used are a mixture of 25 per cent. salt cake (sodium sulphate) and $12\frac{1}{2}$ per cent. "Blue Billy" or burnt iron oxide, of the weight of calcined ore taken. From experimental work carried on, the advantage of an alkaline flux was seen in the complete separation of lead and silver from the slag, which contained practically the whole of the zinc, along with the other constituents of the ore treated, the lead bullion being subsequently cast into "pigs" for desilverization.

In working the furnace, the slag continuously runs from suitably arranged notches into settling pots to allow the depositing of any lead mechanically carried away, and is

then cast in conical moulds for further treatment. This treatment consists of a melting with small coal on the bed of a Siemens open-hearth regenerative gas furnace; by this operation the zinc oxide contained in the slag is volatilised and carried off with the furnace gases to cooling chambers or condensers, and the oxide recovered.

The slag tapped from the furnace settles in two distinct layers, the upper being of no value, and is wheeled away to the tip; the lower forms a kind of matte, and contains any zinc not volatilised in the Siemens furnace, along with iron and soda. It is crushed, calcined, pressed into briquettes, and smelted with fresh ore.

The lead recovery by this process is 90 per cent. in bullion, and the silver recovery in the bullion 80 per cent., the remaining 20 per cent. being recovered from the zinc slag, while the zinc averages 70 per cent. in the form of oxide and matte.

Treating mixed sulphides by a precipitation process has found little or no favour as a practical means of economically working these ores.

Many methods have been devised, amongst which may be mentioned that of Wells, who separates by fractional precipitation lead, copper, zinc, silver, etc., from solutions by means of a soluble alkaline sulphide, added in successive portions. The unroasted ore is first digested with hydrochloric acid in stone vessels, partially neutralised with chalk or lime, boiled, and then filtered through peat. The filtrate is allowed to cool, when most of the lead separates out as chloride, and the remainder is thrown down as an insoluble sulphide by the addition of sodium sulphide. The residue left in the stone vessels is dried, calcined in a reverberatory furnace, and the calcined mass digested with hydrochloric acid, which dissolves out the copper, silver, zinc, and iron as chlorides; the silver is removed as iodide by the addition

of potassium iodide, and the liquor then neutralised with lime.

By fractional precipitation with sodium sulphide, in carefully proportioned quantities, the remaining metals are separated as sulphides.

CHAPTER VI.

CONDENSATION OF LEAD FUME.

TAKING on the average, 1500 cubic feet of smoke per minute is emitted from a reverberatory furnace smelting 1000 tons of ore per annum, and that this smoke contains a good proportion of lead in one form or another, and in a very finely divided state, it can be well understood that, without some means of condensation, these poisonous lead gases, if allowed to go free into the atmosphere, would have a very serious effect on the health of a surrounding community, and in addition be a serious financial loss to the smelter.

This loss may be noted if we consider the value of the products carried off in the course of smelting. Fallize estimates that the lead in the gases emitted from the reverberatory and blast furnaces to be 150 and 130 lb. respectively on every ton of ore, assaying 70 per cent., smelted. Assuming, then, that no means existed for its recovery by deposition in long flues or by wet condensation, the money value of the loss, with lead at £14 per ton, would amount in the reverberatory furnace to 18s. 9d., and in the blast furnace to 16s. 3d. for every ton of ore so treated—a result which no smelter could withstand.

The following two analyses represent the composition of lead fume—

	Alston Moor.	Freiberg.
Lead	trace
Oxide of lead	10·20	27·90
Sulphate of lead . . .	65·60	13·00
Sulphide of lead . . .	1·40	...
Oxide of zinc	13·80	49·50
Oxide of iron	3·40	...
Arsenious acid	2·10
Carbonic acid	7·00
Insoluble in acids . .	5·60	...
	<hr/> 100·00	<hr/> 99·50

The oldest form of arrangement for treating the furnace gases, and which, to a limited extent, is even now used in several English and Continental works, is by a long zigzag vaulted flue, 7 ft. high and 6 ft. wide, and traversing, in some instances, a distance of 5 miles. The large surface friction met with by the travelling gases, condenses more or less completely the volatilised metallic constituents, which gradually increase in bulk, and require a stoppage of the work to effect their removal from the flue.

The modern method of condensation is that in which large chambers are employed, through which the gases are made to circulate about variously arranged condensing surfaces, the operation at the same time being aided by a constant stream of water sufficient to precipitate the matters condensed by the contact surface; or the gases are forced by steam pressure directly through a layer of water, which effects their complete condensation.

In Stokoe's condenser, the gases are forced by a powerful exhaustor into a large chamber built of heavy planking, well tied together with iron rods, and lined internally with enamelled fire-bricks. The chamber is divided into compartments by a number of vertical partitions, open alternately

at the top and bottom, and through which the gases are forced to pass up and down, the condensation being aided by a shower of water kept falling in each compartment down which the gases descend. At the bottom of the chamber is a layer of water rising above the edge of the opening below, so that the gases have to force down the surface of the water and then be driven through it in order to continue their course into the next compartment. Also above the water level are fixed at equal distances horizontal perforated shelves, covered with layers of pebbles or other suitable material, whose surfaces materially assist in the condensation.

Stagg's condenser is similar to the above; the gases, however, are drawn through the chamber by a double-acting pump placed at the end of the condenser.

The arrangement invented by Armand Fallize (*Mineral and Smelting Journal*, vol. ii.) consists of two chambers

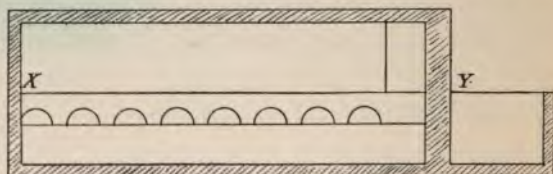


FIG. 17.—Fallize's Condenser. Section through T Z.

A and B (Figs. 17, 18, and 19), the bottoms of which are kept covered by a determined height of water maintained at the level X—Y. The gases enter the chamber A by the extremity E of the flue leading from the furnaces, and pass longitudinally towards the elbow C, by which they enter the chamber B. At *bb*, two jets of steam are injected. On arriving in the chamber B, the gases are thus perfectly saturated with steam, and are besides to some extent cooled partly by the steam, partly by contact with the constantly renewed water in the bottom of the chamber, and partly by

expansion, which results from the difference in the sections of the two chambers. The middle of the chamber B is

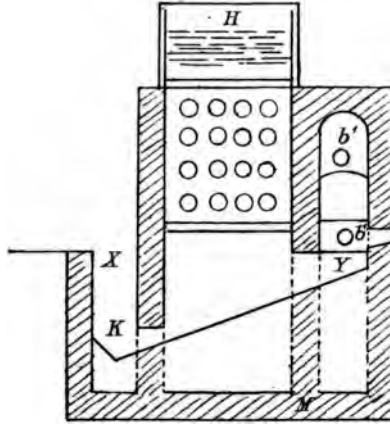


FIG. 18.—Fallize's Condenser. Section through P Q.

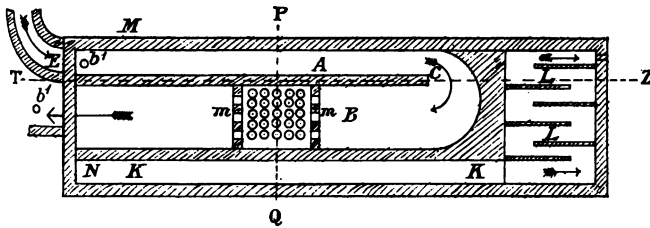


FIG. 19.—Plan.

barred by two vertical intersticed walls *mm*, and in the space between are placed sets of hollow perforated balls. Above this is placed a water tank H, from the perforated bottom of which a shower of cold water falls, which spreads over the surface and interior of the balls. In traversing the interstices of these balls, the gases are cooled, the steam condenses, and the water thus formed, added to the shower of cold water from above, carries to the bottom of the apparatus all the condensable products, whether soluble or insoluble, held in suspension in the gases. The insoluble

matters pass through the stratum of cold water and fall on the inclined bottom, which carries them towards the longitudinal channel K K, where they collect, and can be easily withdrawn by a pump or other suitable arrangement. Any solid particles carried by the current beyond the channel K K are caught in the partitioned pit L L, which the liquid traverses before being discharged. On the other hand, all the matters condensed in the chamber A, or in the chamber B, outside the intersticed walls, are equally brought into the channel K K, for which purpose the walls separating the two chambers are supported by a vaulting, which is kept constantly submerged.

A very efficient condensing arrangement is invented by Hannay, and used in condensing the fumes of sulphate of lead in the manufacture of the white pigment by the White Lead Company Limited. A description of this condenser is given under the heading of Sulphate of Lead.

Softening of Lead by the Calcining Furnace.

Generally, the pig lead produced by the smelting of the ore is of a hard nature, and unsuitable for desilverizing or conversion into white lead, or into sheets, pipes, etc. This hardness is due to the presence, in more or less proportions, of antimony, arsenic, copper, iron, and other metals, and for their removal the process of calcination is resorted to, which is simply an oxidation of these metals, along with a small portion of the lead, the whole forming a scum on the surface of the molten metal in the calcining pan, and can thus easily be removed. The calcining is carried on until a sample withdrawn has all the properties of a "soft" lead. The scum is smelted for the recovery of the lead.

In the following analyses the composition of some non-silveriferous hard leads of English, Spanish, and Austrian make are given :—

	English.	Spanish.	Austrian.	
Analyst . . .	Richardson.		Freiberg. Karsten.	Clausthal. Streng.
Lead . . .	99·27	95·81	91·51	85·34
Antimony . . .	0·57	3·36	5·32	14·06
Arsenic	1·02	...
Copper . . .	0·12	0·32	0·90	...
Iron . . .	0·04	0·21	0·62	0·10
Zinc . . .				
Sulphur	0·20	...
	100·00	99·70	99·57	99·50

The form of furnace used for softening hard lead is of the reverberatory type, elevation and section being shown in

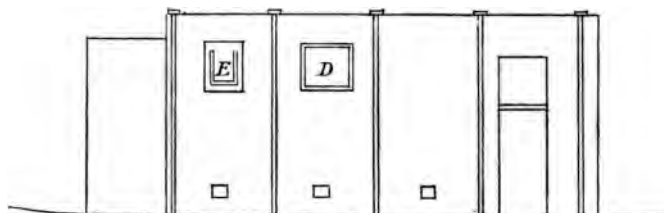


FIG. 20.—Softening Furnace. Elevation.

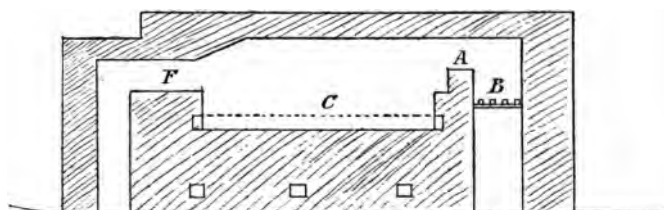


FIG. 21.—Section.

Figs. 20 and 21. It is built of fire-brick, and tied with tie-rods, with the usual bridge A and fire-place B. The hearth C consists of a wrought-iron pan in which the charge of lead is treated, D is the working door, E the spout for running off

the soft lead, and F is a flue carrying away the spent gases. In some works, the charge is added to the pan in the form of pig lead; in others it is previously melted and then ladled into a spout, which carries it to the pan. An improvement over these methods of charging, consists in heating the lead in a large cast-iron pot embedded in brickwork, placed at the end of the furnace, and at an elevation so that the molten metal can be run as required direct into the pan, the waste heat of the furnace being used for heating the pot. The weight of a charge will vary from 10 to 30 tons.

The process of liquation depends on a separation of different metals, according to their melting-points; and on this principle is based the working of the calcining furnace. The charge is first subjected to a temperature sufficient to melt the lead, which liquates out from the metals of a higher melting-point, which, rising to the surface, becomes oxidised as the temperature of the furnace is increased, and, forming a scum with the oxide of lead present, is removed from time to time. To render the scum less pasty, and thus facilitate its removal, a little lime is thrown on the surface, which acts as a dryer. After eight to nine hours' exposure a sample of the molten lead is drawn, cooled, and then examined. If the cooling is accompanied with a deep blue film on the surface of the sample, and the metal, when solid, is soft to the scratch, the treatment is considered as finished, and the contents of the pan are tapped off into moulds as soft pig lead for further treatment by the Pattison, Parkes, or the Luce-Rozan desilverizing process. The following are the average yields of soft lead by the calcining process (Payen):—

From	Yield of Soft Lead.
Good Spanish hard lead . . .	93·2 per cent.
Hard lead from crystallizing dross . . .	90·3 „
English slag lead . . .	87·1 „
Slag lead from refuse products . . .	67·3 „

the cost of treatment being about 3s. 5d. per ton for labour, coals, and repairs.

According to Keith, the refining of lead is now carried out by electrolysis in New York (1892) by the Electro Metal-Refining Company.

In each of the thirty wooden vessels, 3 ft. deep and 6 ft. wide, dip 13 cylinders of thin brass plate, arranged concentrically at about 2 in. distance from each other, and serving as cathodes. The anodes are formed of plates of unrefined lead, each being 2 ft. \times 6 in. \times $\frac{1}{8}$ in., surrounded by muslin bags. A solution of sulphate of lead with acetate of soda is constantly fed into the vessels at the bottom, and runs over at the top into a warming apparatus, where it is heated to 38° C. (100° F.), and is then conveyed back into the electrolysing vessels. Arsenic, antimony, silver, etc., are deposited in the muslin bags surrounding the anodes, and are melted with saltpetre and soda to obtain the silver. Practically, all the impurities are removed from the hard lead by this process.

CHAPTER VII.

DESILVERIZATION ; OR, THE SEPARATION OF SILVER FROM ARGENTIFEROUS LEAD.

IN the olden days of lead-smelting, the separation of the silver was carried out by converting the whole of the lead into oxide, and thence recovering the silver by cupellation, the oxide ultimately being re-smelted with carbonaceous matter to recover the lead. The process was very wasteful in lead, and a portion of the silver remained unrecovered, which gave to the lead a certain hardness, which depreciated considerably its market value. Later, this method of treatment gave way to the Pattison, the Luce-Rozan, or the Parkes process of desilverization.

The Pattison Method of Treating Argentiferous Lead.—This method is based on the property of lead to crystallize out from its molten state, up to a certain point, leaving the silver to form what is termed a eutectic alloy with the remaining lead, and containing the former to the extent of 500 to 600 oz. to the ton. If, therefore, an argentiferous lead is melted and then slowly cooled, the larger portion of the lead can be removed by crystallization, leaving practically the whole of the silver as a rich alloy, from whence it is recovered, by the process of cupellation.

In practically carrying out this principle, the "Pattisonisation" is rarely carried to more than 500 oz. silver to the ton.

For working the process, a series of cast-iron pots, holding 8 to 9 tons, are incased in brick

fire-place is provided for each pot. In Fig. 22 an installation is shown of eleven pots working what is termed the "high system." Between each pair of pans a smaller pan is placed, which is kept full of molten lead, and is used for cleaning the perforated ladle. Pot No. 1 receives the rich silver-lead alloy at the end of the process, while pot No. 11 is termed the market pot, from whence the desilverized lead is cast into pigs for various uses in the arts.

Starting, say, with a lead containing 16 oz. silver to the ton, it is first melted in pot No. 6, the dross skimmed off, and then allowed to partially cool by withdrawing the fire. During the cooling the charge is constantly stirred, and any portion which solidifies round the edges is removed by an iron "slice," and mixed with the molten lead. As the temperature lowers, the crystals of lead increase in bulk, and are removed from time to time by the perforated ladle, supported by a swinging crane, and, after draining, are emptied into pot No. 7. This is continued until two-thirds of the metal, in the form of crystals, has been removed; the remaining one-third liquid portion is then transferred to pot No. 5, and contains about double the quantity of silver that existed in the original charge, while the crystals of lead are poorer to the extent of one-half. The same operation is repeated with all the intermediate pots, fresh lead, having the same percentage of silver, being added to each pot to make up the bulk, until the rich silver alloy reaches pot No. 1 and the desilverized lead-pot No. 11. The series of pots will show the following assays of silver per ton:—

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	No. 6.
Silver-lead alloy.	512 oz.	256 oz.	128 oz.	64 oz.	32 oz.	16 oz.
	per ton.	per ton.	per ton.	per ton.	per ton.	per ton.
No. 7.	No. 8.	No. 9.	No. 10.	No. 11.		
8 oz.	4 oz.	2 oz.	1 oz.	$\frac{1}{2}$ oz.	Market lead.	
per ton.	per ton.	per ton.	per ton.	per ton.		

The method of working depends on the amount of silver in the lead to be desilverized. With poor argentiferous leads the "low system" is adopted, being the removal of seven-eighths of the contents of each pot in the form of lead crystals; with richer leads containing 15 to 30 oz. silver to the ton, the "high system" is in use, and which depends on the conversion only of two-thirds of the charge into crystals, the silver doubling itself in each operation. During the working, the skimmings or dross taken from the surface of the molten metal in the pots averages about 25 per cent. of the weight of the original charge, and is set aside for reduction to metallic lead in the reverberatory furnace.

The Luce-Rozan Process.—This method, used largely in France, is a modification of the Pattison treatment, and depends on the use of steam for agitation during the crystallizing out of the lead. By its use, the softening of the lead, previous to its desilverization, is dispensed with, the antimony, arsenic, iron, zinc, etc., being removed in an oxidised state by the action of the steam. The size of the plant varies according to the output required, consisting, in some works, of a large pot holding 20 tons of lead, and heated by a fire-place underneath. In conjunction with this, and at a lower level, is placed the crystallizing pot, having a capacity of some 40 tons. In desilverizing, the charge of argentiferous lead is first melted in the upper pot, and thence run by a spout into the lower, among the crystals left by the last charge, which rapidly liquefy. The surface of the molten mass is now skimmed, the skimmings being laid aside for reduction, and a jet of steam introduced in the bottom of the pan, and which is evenly spread by means of a suitably arranged baffleplate above the nozzle. Gradually the temperature falls, and the formation of crystals commences through the molten mass. This is continued until two-thirds of the charge have crystallized, leaving the remainder, or one-

third, in a liquid state, the separation being effected by draining off the latter through perforated plates, the crystals being retained in the pot. A fresh charge of lead, having the same percentage of silver as the crystals, is then run in, and the steaming operation repeated. The liquid portion drained from the crystals, after cooling, undergoes the further process of cupellation, for recovery of the silver, while the crystals in due course are melted and cast as market lead.

The Parkes Process.—This interesting method depends upon the physical fact that silver alloys itself more readily with zinc than with lead, and that a mixture of zinc and lead, in any proportion, will not form an alloy on fusion, the two metals separating out in distinct layers on cooling. If, then, argentiferous lead is melted and the bath treated with molten zinc, the silver from its greater affinity becomes attached to the zinc, and on cooling the bath the argentiferous zinc separates on the surface as a distinct layer from the lead.

The process is carried on in large hemispherical cast-iron pans placed in close proximity to the calcining furnaces, from whence the lead can be run direct into the pans. A charge of about 20 tons is usually given each pan, which is incased in brickwork and heated by a fire beneath. At a temperature of 420° C. the zinc is added, in proportion varying with the amount of silver present, a charge containing 30 oz. silver to the ton requiring about 1 per cent. of zinc, which is well stirred into the molten mass with iron rabbles. On complete solution, the contents are kept at the above temperature for twenty minutes, and then gradually cooled by damping the fire. Below 418° C. the zinc begins to solidify, forming a crust on the surface, and carrying with it practically the whole of the silver.

The crusts as they are formed are removed, and finally the lead, while still retaining a small percentage of zinc, becomes practically desilverized. To eliminate the zinc, the

lead is remelted in the calcining furnace, the former metal being oxidised and then volatilised as zinc oxide.

The silver-zinc crusts with a proportion of mechanically mixed lead are now treated by the process of liquation, to remove a portion of the latter. By this operation, which is carried on in an iron pot heated by a separate fire, the temperature is raised to a point slightly above the melting-point of lead, and the excess of the latter "sweated" out, the metal flowing to an adjacent lead-pot.

For recovery of the zinc and silver the residual mass in the liquating pot is mixed with charcoal, and then charged into retorts or crucibles, and the zinc distilled over and condensed (see Zinc). The residue of the retorts, consisting of silver and lead, is cupelled to obtain the precious metal. In some German works, the zinc crusts are mixed with lead chloride, and the mass heated to a dull redness. The soluble zinc chloride formed is washed out, leaving an alloy of silver and lead, which is cupelled for the recovery of the silver.

The following analyses represent the composition of desilverized and market leads :—

	English.	German.	Spanish.
Lead	99·989	99·927	99·892
Antimony	0·006	0·018	0·036
Copper	0·009	0·017
Zinc	0·002	0·020	0·035
Iron	0·003	0·024	0·019
	100·000	99·998	99·999

Cupellation.—The rich silver-lead obtained by any of the three methods described above requires to undergo the process of cupellation, to effect the separation of the valuable metal from the lead. Cupellation depends on the easy conversion of metallic lead in a molten state and in contact with

a current of air to oxide of lead or litharge, while the silver remains entirely unchanged. Two systems of cupelling are in use—the English and the German. With the former, the furnace used is of the reverberatory type with fixed roof, and the cupel or test in which the silver-lead is treated is movable, the charge being fed at intervals during the refining. The latter system, on the other hand, is carried on in a form of furnace in which the roof is made of iron, and can be removed as required by a crane; and, unlike the English method, the cupel is a fixture in the bed of the furnace, while the charge of silver-lead is not distributed over the working, but is made in full at the commencement.

English System of Cupellation.—The reverberatory furnace used is sometimes erected singly or in pairs, in which two cupels can be worked at the operation. In Figs. 23 and 24 a section and plan are shown of a double-cupelling furnace. AA are the fire-places; BB the fire-bridges; CC the cupels resting on the waggons DD; EE are the lead-pots containing the silver-lead, and which supply the cupels by means of the iron gutters FF; GG represent the tuyeres supplying the blast; at HH are openings in the cupels through which the litharge formed is blown over into the receivers below; II are the flues for carrying off the gases; and KK the double-chimney.

The cupels used are oval or rectangular in shape, each consisting of an iron frame 4 ft. long and $2\frac{1}{2}$ ft. wide, the bottom being formed of iron bars bolted on to the framework. They were formerly filled with powdered bone-ash moistened with carbonate of potash, and then beaten down to form a solid compact mass. According to A. K. Huntington, this is now superseded by a cheaper mixture of clay and limestone, which, after pressing, is scooped out so as to form a cavity, and leaving a lining of the mixture round the sides and bottom of the iron frame. In the front, a channel some

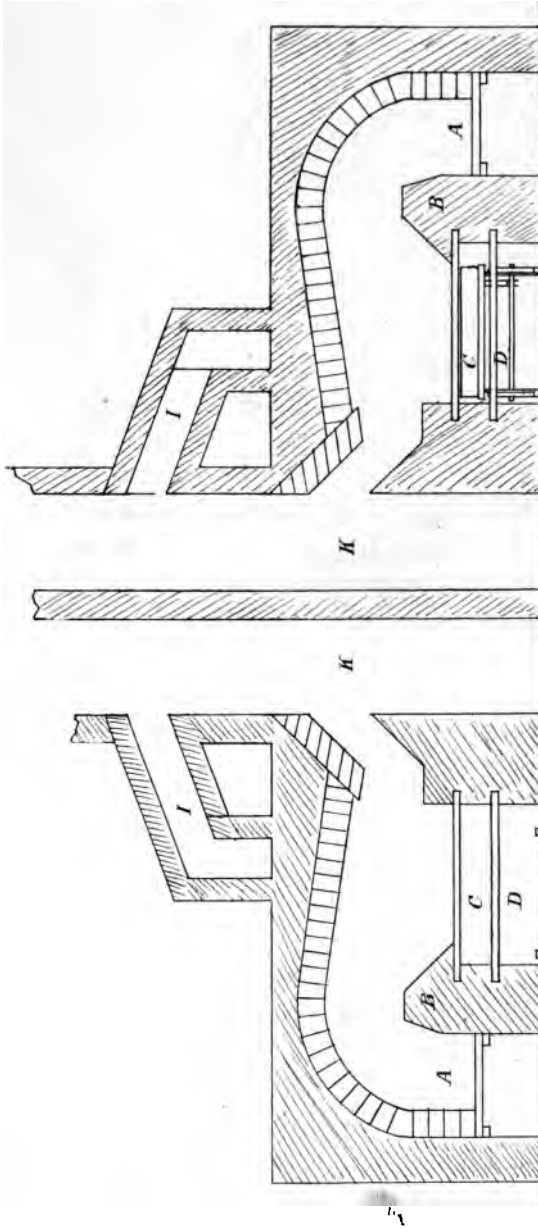


FIG. 23. —Double-Cupelling Furnace. Section.

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5 in. in width, whereby the molten litharge can flow through into the receiver below. The cupel forms the

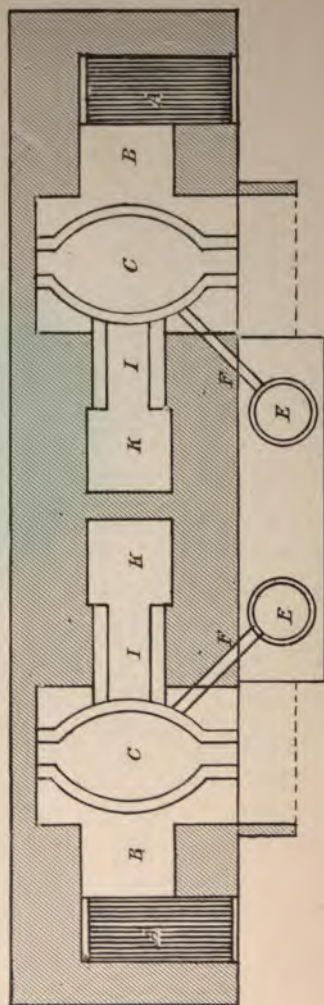


FIG. 24.—Double Cupelling Furnace. Plan.

hearth of the furnace, and, resting on a carriage, can be removed, and a new one replaced, without interfering with the working of the furnace.

CHAPTER IX

PROTOXIDE OF LEAD—LITHARGE AND MASSICOT.

PROTOXIDE of lead, which occurs in the native state as lead ochre, is formed by the chemical union of lead with oxygen. It is brought into commerce as litharge and massicot, the former being crystalline in its texture and of a reddish-yellow colour, the latter an amorphous yellow powder. The two, though differing in certain of their physical properties, are yet identically the same in chemical composition.

They are used for the preparation of drying oils and for assaying and pharmaceutical purposes. When mixed with other ingredients and the mixture ground with linseed oil in a mill to a stiff paste, they form a very durable cement for stone work. Litharge in a flake or levigated form, is also used in the manufacture of acetate and other lead compounds, and as a glaze for earthenware.

Litharge.—On the large scale, litharge is either obtained as a bye-product in cupellation, or is produced directly by the oxidation of molten lead in the hearth of a reverberatory furnace, the temperature being raised to melt the resulting oxide and so convert it into the reddish-yellow litharge.

From the first cupellation, the litharge obtained contains a proportion of silver, and to recover this it is reduced to the metal which is treated by the Pattison or the Parkes process, the silver-lead alloy being again cupelled. The litharge from the second cupellation is collected in large pots; the first and last portions are generally rejected as

being too impure for marketable purposes. The gradual cooling is a matter of importance, as the proportion of flake litharge yielded depends on this condition. On emptying the cooled pots, the friable portion is crushed and passed through a revolving circular screen enclosed in a wooden erection, and the fine flake litharge collected and packed in casks for the market.

The hard and coherent mass remaining is used for the manufacture of levigated litharge, and for this purpose it is fed with water into a set of millstones, the ground material thence falling into tubs below and well agitated with water by means of revolving paddles, to wash and separate the coarser particles. The washed litharge is now run into large settling tanks, allowed to subside, and the supernatant water syphoned off, leaving a thick layer of reddish-yellow oxide for drying. At some works, the water and litharge are pumped direct into powerful filter-presses, thus effecting a better separation than by settling of the two, the cakes of litharge produced containing less than 8 per cent. of moisture. By either way of treatment, the litharge requires to be dried, and this is carried out by exposure to the low heat of a reverberatory furnace for several hours. The dried product is packed in casks and sold as levigated litharge.

Massicot.—When nitrate, carbonate, or oxalate of lead are heated in contact with air, and at a temperature while sufficient to break up these bodies, yet insufficient to melt the oxide produced from their decomposition, a lemon-yellow powder results, and to this the name of massicot is given. On the large scale, it is prepared by melted refined lead on the flat hearth of a reverberatory furnace, at a temperature low enough to prevent the fusing of the oxide of lead formed. This is removed as it forms on the surface, and the operation is continued until practically the whole of the molten lead is converted into a yellow amorphous powder, which is ground,

washed, and dried in a manner similar to the treatment of litharge.

The manufacture of marketable litharge direct from the ore is carried out by a process invented by Fell (New York, 1900). He converts the galena (sulphide of lead) into sulphate of lead, by mixing the powdered ore with some refractory material, also in powder, such as lime or magnesia. This mixture is then carefully heated for about one hour in a reverberatory furnace at a temperature ranging from 600° to 750° F., with excess of oxygen so as to oxidise both the lead and the sulphur of the ore. This heating converts the lead in the charge wholly or partially into sulphate of lead. On completion of the oxidation, it is withdrawn from the furnace, cooled, and then intimately mixed with dry powdery caustic soda in the proportion of 26 parts caustic soda to 100 of sulphide of lead, and the mixture submitted to heat; the caustic soda converts the oxidised sulphur compounds into protoxide of lead and sulphate of soda.

The mass now consists of protoxide of lead, mixed with some undecomposed ore, matrix, and sulphate of soda, which is put into suitable vessels, and water added to dissolve out the soluble soda salt; the whole is then allowed to settle, and the clear liquor decanted. The undissolved residue is now treated with a strong solution of caustic soda (1 part to 2 parts water), and brought to the boiling-point with constant stirring. On turning off the steam and allowing to settle, the clear liquor containing the whole of the protoxide of lead is run into a vessel containing metallic lead in such form as to present as much surface as possible. In practice, granulated or spongy lead formed by pouring molten lead into water is employed. The hot solution of the protoxide is allowed to remain for a short time, and is then drawn off to another vessel to cool, and as it cools it deposits the litharge in the form of crystals, which vary in size and colour

by the Pattison or Parkes process for any silver it may contain.

The refined and desilverized metal now appears in commerce as market lead with less than 0.02 per cent. of impurities, and is used for conversion into pipes, sheets, pigments, and other purposes.

CHAPTER VIII.

THE MANUFACTURE OF LEAD PIPES AND SHEETS.

THE conversion of soft lead into pipes and sheets is a very important branch of industry, and requires a high standard of purity in the metal used. For manufacturing pipes (*Scientific American*, April 1895), the refined metal is cast into pigs 50 to 100 lb. in weight. They average about 3 in. in thickness, and range in length from $1\frac{1}{2}$ to 3 ft. The first operation is the smelting of about forty pigs in a kettle incased in a fire-brick furnace about 4 ft. square, the kettle being made of cast-iron about 2 ft. 3 in. in diameter, 2 ft. 3 in. in depth, and about $\frac{3}{4}$ in. in thickness. It is flanged on the top, and rests on an iron frame. Connected to the outside, near the bottom of the kettle, is a 4-in. iron pipe or spout, through which the molten lead is passed into the cylinder of the hydraulic lead-press. This operation is performed by means of a perpendicular shaft attached to one side of the interior of the kettle, connected to the bottom of which is a conical-shaped valve, which fits snugly into a circular opening in an iron seat leading to the pipe at the bottom. The shaft, which has a toothed pulley at the top, connects itself by means of a belt chain to another on the outside of the furnace. When the cylinder of the press is to be filled with molten lead, the operator turns the outside shaft, which, by means of the belt chain, turns the other on the inside of the kettle, a thread at the top of the shaft causing the valve to rise, letting out the molten material

layers of metallic lead. The metal used requires to be the finest quality, very soft, and free from copper or antimony, the former colouring the pigment a dull grey. Bannow and Kraemer state that the pinkish tinge occasionally seen in the manufacture, is due to the presence of small quantities of lead suboxide.

The process is carried on in large stacks, varying in size in different works, some being, according to Bedson, 28

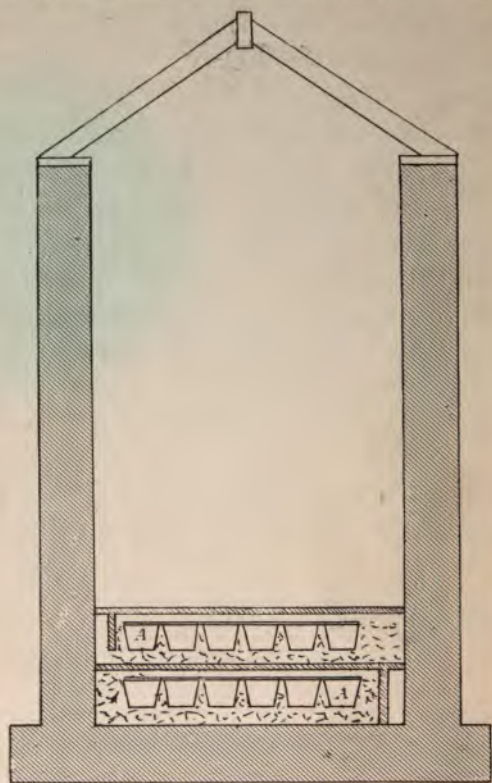


FIG. 26.—White-Lead Stack, showing arrangement of Pots A A. Section.

high and 14 ft. square, with a lead capacity of 84 tons (Fig. 26). The first stage in the manufacture is the p

for chemical manufacturing work, and for flushings, gutters, ridges, and other roofing purposes, sheet lead finds an extensive use.

The pigs of desilverized lead are first melted in a large iron kettle having a capacity of 10 to 12 tons, and similar in construction to the one used in the manufacture of piping above described. A spout connects the kettle with a mould holding about $4\frac{1}{2}$ tons, and having a size about 5 ft. in length, and 7 ft. 10 in. in width. Lifting hooks are placed at each corner, and the molten metal is then run into the full capacity of the mould. After three days the flat ingot formed is sufficiently cooled to be raised by a travelling crane and carried direct to the rolling mill, which consists of double-cylinders 9 ft. long and 30 in. in diameter, geared directly to the main driving engine, and provided with the adjustments common to all rolls.

The table or bed of the mill is composed of a double series of parallel rollers, on which the lead rests, and the necessary motion is obtained by a rack adjustment placed between the parallel lines of rollers, whereby it is pushed between the cylinders. The ingot is passed and repassed until the length has increased to 30 ft., the width remaining constant, and weighing about 30 lb. to the square foot. To reduce the sheet into a length and weight per square foot required for commerce, it is cut into sections by vertical knives working across the bed between two of the supporting rollers. Each section is again rolled into 18-ft. lengths, and of a weight varying from $2\frac{1}{2}$ to 10 lb. per square foot, according to requirements.

Tea Lead.—This form of lead, existing in very thin sheets, is exclusively used for lining tea-chests, and in its manufacture employs considerable native labour in Hong Kong and Shanghai. The process consists of pressing between tiles faced with several thicknesses of unsized paper a right pro-

each alternate end to allow the circulation of air through the stack. On this is placed another layer of tan to a depth only of about 1 ft., which forms the second bed, and on it the layers of pots and lead are placed, as in the first bed. The stack is thus gradually built to the top of the brick chamber, the front opening closed up and then allowed to stand fourteen to fifteen weeks before reopening.

During this period, the various chemical actions which transform the metallic lead into a definite mixture of carbonate and hydrate of lead take place. From the fermenting tan is obtained, along with carbonic acid, the necessary heat to volatilise the acetic acid and water in the pots; and these products in conjunction with the oxygen of the air in the stack, acting upon the lead, yield a basic acetate, which is further converted into basic carbonate of lead by the action of the moist and warm carbonic acid. When the corroding action is deemed sufficient, the stack is reopened and the plates are found covered with a thick coating of white lead. To detach this from the cores of uncorroded lead, the white layers are carefully removed and thrown into large tanks containing water, and from thence are lifted by a bucket elevator to an endless band, which feeds two pairs of rollers; on passing through the last pair, the detached metal falls into a receiving tank, while the powdery white lead drops over a sloping shelf into another tank, to be ground and then dried for the market.

The lead is again melted and cast into plates or grates for a second corrosion.

In grinding the wet white lead to a condition suitable for drying, six or seven pairs of stones are used in some works, the pulp being passed through the series before a sufficient degree of fineness has been attained.

The drying is carried out in long brick chambers, pro-

vided with ventilators for carrying off the moist air. On each side of the central passage are arranged the wooden racks for supporting the shallow dishes containing the pulp lead. The chambers are warmed by air flues, and kept at a temperature which, while it effectually dries the white lead, does not injure its colour. Over-heating gives a yellow coloration to the pigment, which depreciates its value.

White lead is very quickly attacked by sulphur compounds, forming black sulphide of lead. Consequently, when used in a sulphuretted atmosphere, it does not retain its colour in the same manner that zinc white would do under similar conditions.

When white lead is strongly heated in contact with the atmosphere, it forms a variety of red lead, having an orange tint, and known commercially as orange lead.

Heavy spar, gypsum, zinc oxide, and sulphide are frequently used as adulterants in commercial white lead, and lower its value as a pigment.

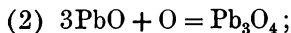
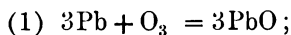
Red Lead or Minium.

Red lead or minium is a combination of peroxide with protoxide of lead—



and exists as a scarlet crystalline powder, with a specific gravity of 8.62.

It is prepared by the oxidation of metallic lead into protoxide or litharge, and thence into red lead by a further absorption of oxygen—

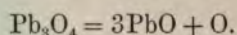


the theoretical yield being 110.36 parts from 100 parts of metallic lead oxidised, or 10.36 per cent.

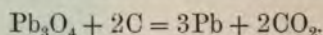
According to Percy, commercial red lead has the following composition:—

Red lead {	Peroxide of lead	18.89
	Protoxide of lead	80.54
	Sesquioxide of iron	0.19
	Copper and silver	trace
		<hr/>
		99.62

Red lead, when heated, changes from scarlet to a violet colour; the original shade, however, is regained on cooling. At a red heat it is decomposed into oxygen and litharge, thus—



Like all the other oxides of lead, it is quickly reduced to metallic lead when heated to redness with charcoal—



The manufacture is carried on in two stages, the first being the conversion of the lead into litharge, and technically known as “drossing”; and the second consists of a further heating of the litharge until the desired colour is obtained, and is known as the “colouring” stage. Some manufacturers conduct both processes alternately in the same furnace or oven; others, again, use a second furnace for the colouring.

In construction, both furnaces differ but slightly, and are seen in elevation and plan, Figs. 27 and 28. They are built of fire-brick, well tied by standards and tie-rods, and both have low-arched roofs. The bed of each furnace is made of fire-brick, and slightly inclines from each side towards the centre, being supported by a cast-iron bed-plate resting on brick columns. In Fig. 27 the three front openings necessary for working the furnace are shown; A A being the fire-places, and B the door through which the charge is made and the rabbling of the molten metal effected for oxidation; the chimney C carries away the gases and any lead fume.

A charge of 28 cwt. is used, comprising 25 cwt. of pig lead with 3 cwt. of unoxidised lead from previous workings, and the fuel consumed is a good quality slack.

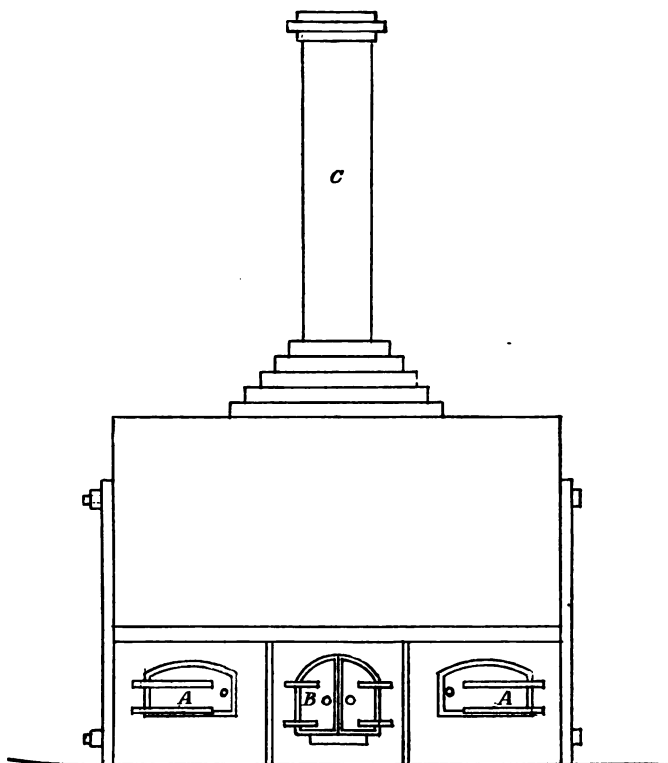


FIG. 27.—Dropping Oven. Elevation.

In working, the furnaceman first builds a low dam across the front of his oven with ground and levigated oxide from a previous charge, and behind this barrier the pigs of lead are placed. The metal soon melts, forming a pool, which is vigorously rabbled, so that every part shall in turn be presented to the oxidising flame. This continues for three hours, and the litharge produced is thrown back, forming a heap at the back of the furnace. After eight hours' exposure

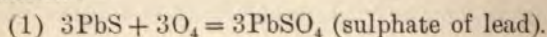
in France, the finished pigment being known as "Clichy White." It is made by dissolving litharge in acetic acid, and then passing into the acetate formed, a current of carbonic acid gas. When first brought out, it was considered to be a revolutionary process, and likely to supersede the old method; but it soon became apparent that the pigment had not the capacity or body of Dutch lead,—in other words, it was crystalline in texture, and not amorphous.

Later, Dale and Milner (1872) produced a pigment by agitating litharge, salt, and water together, so as to form an insoluble basic chloride of lead, and suspending this product in a solution, made by dissolving caustic soda and common salt together; the precipitate was then finally treated with carbonic acid in a lead-lined vessel.

Wilson (1884) first produces a basic acetate of lead by the alternate action of air, steam, and normal acetate of lead, upon finely divided lead contained in a revolving drum. The basic acetate is then removed to another vessel and treated with carbonic acid gas, yielding a mixture of carbonate and hydrate of lead.

Lowe (1887) forms a lead nitrate by dissolving litharge in nitric acid, and thence precipitating from the solution a normal carbonate of lead by adding bicarbonate of soda or potash. To convert the normal into the basic product, he adds a basic lead acetate to the former.

Bonner (1889) first prepares a sulphate of lead by precipitation with sulphuric acid, or oxidises in a current of air, galena ore; the resulting sulphate is then converted into the basic form $2\text{PbSO}_4 \cdot \text{PbH}_2\text{O}_2$, by boiling with caustic soda. On washing the precipitate to free it from sulphate of soda, it is further heated with carbonate of soda, basic white lead being formed. The reactions are seen in the following equations:—



furnace, of which a plan is seen in Fig. 28. Here it is exposed on the bed D with constant stirring to a temperature ranging from 550° to 600° F., the furnace doors being open to allow a plentiful supply of oxygen. At the end of forty-five hours' exposure, a drawn sample on cooling should have the characteristic scarlet colour of red lead. The doors are now closed, and the furnace allowed to cool slowly—a provision necessary to the success of the colouring stage; then the charge is withdrawn, ground and sifted for the market. The increase in weight averages 8 per cent., showing a loss of over $2\frac{1}{4}$ per cent. in working the two stages.

Red lead of commerce is sometimes found adulterated with brick-dust and iron oxide; these impurities can be detected on heating the sample, which, if pure, would assume the yellow tint of litharge, and, if adulterated, the red colour of brick-dust and ferric oxide would remain permanent under the heat.

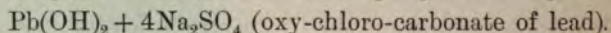
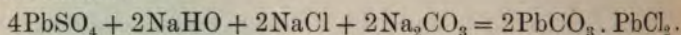
The requisites for a good protective covering for iron and steel, are stated by Mr. William Jones to be—

- (1) That it should firmly adhere to the surface, and not chip or peel off.
- (2) It must not corrode the iron, else the remedy may only aggravate the disease.
- (3) It must form a surface hard enough to resist frictional influences, yet elastic enough to conform to the expansion and contraction of the metal, by heat or cold.
- (4) It must be impervious to and unaffected by moisture, atmospheric and other influences, to which it may be exposed.

In undertaking to produce a paint having these requirements, Custer and Smith (1896) consider that there is not paint in existence that will meet these wants so fully as good red lead, ground in linseed oil, when applied in two coats, and which yield an absolutely impervious and water-

the contents of the vessel well agitated until basic white lead is formed. This product is now forced on to filters, to separate the white sludge from the fluids, and then dried in the usual way.

Gamelin (1896) suggests the use of a new pigment in the form of oxy-chloro-carbonate of lead. It is prepared by heating a mixture of lead sulphate, caustic soda, common salt, and carbonate of soda, in water to 100°C .; the precipitate formed is then thrown on to a filter, washed free of sulphate of soda, and then dried. The following equation represents the reaction:—



Galloway (1397) forms a white pigment of lead, by heating a mixture of silica and nitrate of soda with superheated steam, nitric acid being given off. The acid is led into earthenware pipes or stone towers containing scrap lead, or litharge, whereby nitrate of lead is formed. This is neutralised with ammonia, and precipitated by treatment under pressure with ammonia and carbonic acid, or with ammonium carbonate direct. The resulting white precipitate, is a basic carbonate of lead, which, after washing free from ammonium nitrate, is dried.

(a) *Carbonate of Lead by Electrolysis.*—The application of electricity in the manufacture of white lead is a new departure, and finds considerable favour in the United States. In this country, it is believed that the pigment produced is not free from that crystalline character which is fatal to all lead compounds, in their attempts to supersede Dutch white lead.

In describing the Brown electrolytic process, Mr. R. P. Williams says it consists of—

- (1) The electrical preparation of nitric acid and caustic soda ;

CHAPTER X.

LEAD POISONING.

Of all the lead compounds used as white pigments, lead sulphate is the only one which is non-poisonous in its action on the system. This property is due to the insolubility of the pigment in the gastric juices of the stomach, and consequently it passes away into the bowels without change. On the other hand, all the carbonates, whether made by the precipitation or the Dutch process, are rendered soluble by such action, and consequently, in this soluble form, pass into the blood. Hence the evil effects to the workpeople engaged in this class of work, although the Home Office has done much to mitigate the dangers of the work by enforcing stringent regulations in the conducting of white-lead factories.

White lead in the form of a fine dust is taken into the system, partly through the lungs, and partly by absorption through the skin, which in time produces what is termed, chronic lead poisoning. One of the earliest indications of the trouble is seen in the blue line on the gum, and this is generally accompanied by great constipation. Then follows acute pains in the pit of the stomach, and the skin becomes clammy with cold perspiration. The sufferers may recover completely, or may be affected, says Dr. Rabagliati, by the second form of chronic poisoning known as lead palsy. In some instances it terminates in a species of apoplexy, which comes on with giddiness, extreme weakness, and torpor. As

these increase, the pains in the abdomen subside, and the patient at length dies, convulsed and comatose.

In the treatment of mild cases, Epsom salts dissolved in a little water and flavoured with liquorice, forms a good antidote, the sulphuric acid forming with the lead an insoluble sulphate of lead, which passes into the bowels and is thus removed. In chronic cases, potassium iodide is administered three or four times a day, the action by this treatment being the formation of a yellow insoluble iodide of lead.

The regulations controlling white-lead factories are applicable both to employers and employed. In the first place, the former are required—

(1) To provide respirators, overall suits, and head-coverings for their workpeople, and to see, through the managers or foremen, that they are delivered to and worn by each person engaged;

(2) To provide bath accommodation with hot and cold water, soap, brushes, and a daily supply of clean towels for both male and female workers;

(3) To provide dressing-rooms, dining-rooms, and cloak-rooms;

(4) To allow ten minutes before each meal-time and at the close of the day's work, for changing of clothes and washing;

(5) To provide for the weekly visit of a doctor, and to keep a register of all employed, and when examined by the doctor;

(6) To see that no female is employed without a medical certificate;

(7) To report any case of illness from lead poisoning to the H.M. Inspector for the district and the certifying surgeon;

(8) To supply certain sanitary drinks for the use of the workpeople;

(9) To see that every stack is fitted with stand-pipe or movable hose provided with a very fine rose, so that a supply of water can be distributed ;

(10) To see that each department of the factory is well ventilated, so that any lead-dust can be carried away.

As regards the workpeople, the regulations require—

(1) That each person, before commencing work, sees that he has served out to him, respirators, overalls, and head-coverings whenever required, either in the “ blue ” or “ white ” beds ;

(2) That each man or woman, before going home or to meals, must put off their overalls, etc., and deliver them to an attendant ;

(3) That each man or woman brush off every particle of lead from their clothes, thoroughly wash, and see that no dust remains under the finger-nails ;

(4) To regularly take the sanitary drinks provided.

CHAPTER XI.

LEAD SUBSTITUTES.

STRICTLY speaking, only those pigments containing lead as a basis may be rightly considered as genuine substitutes for Dutch white lead. Many substitutes have, however, been proposed and used with more or less success which contain no carbonate of lead, and others again in which the value of the lead pigment is lowered by the addition of native or precipitated sulphates or carbonates of barium, strontium, lime, magnesia, etc.

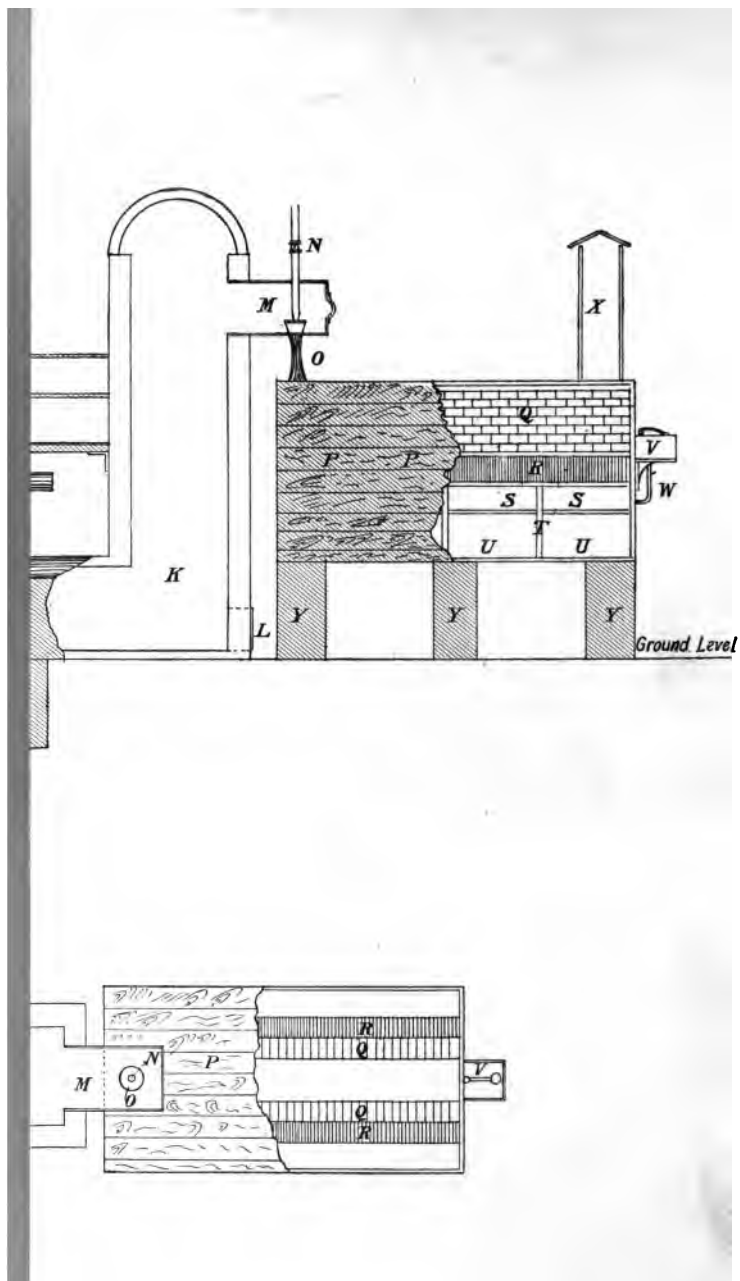
Under this heading, then, will be described—

- (1) Substitutes of which lead forms the basis.
- (2) Substitutes used as pigments, but containing no lead.
- (3) Substitutes in which the value of the lead compound present is lowered by the addition of native or precipitated sulphates or carbonates of barium, strontium, lime, magnesia, etc.

1. Substitutes of which Lead forms the Basis.

In the form of a spongy, transparent, globular powder, or in a crystalline condition, are found the particles of all lead pigments. On this difference, which is dependent on the mode of manufacture, depends the permanence and covering power of the pigment.

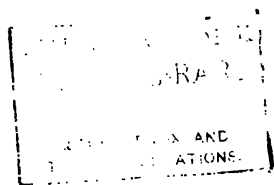
A white lead made by the old Dutch process is of the globular variety, and is found, when ground with linseed oil, to absorb more of the oil than the white lead, having a crystalline texture, and practice has shown that it has



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fume; the steam, escaping condensation, being driven through the interstices of the fire-clay slabs, to the sides of the condenser, whence it escapes at the end through the chimney. A continuous fall of lead sulphate thus takes place to the bottom of the condenser, from which it is removed by the pump.

The product thus produced contains, in addition to sulphate of lead, the oxides of lead, zinc, and iron. To convert

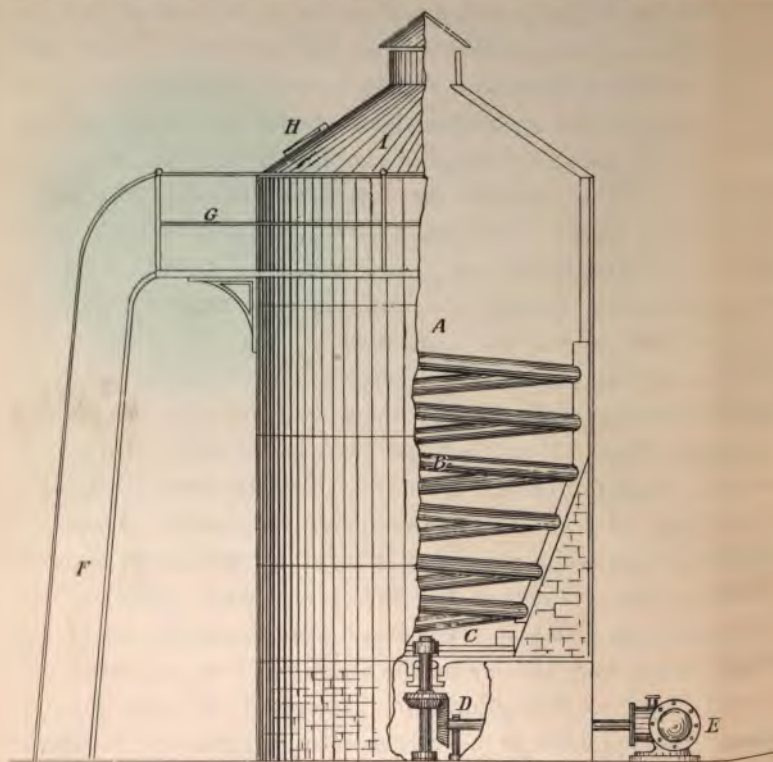


FIG. 31.—Sectional Elevation Lead Washer.

the oxide of lead into insoluble sulphate, and the oxide of zinc and iron into soluble sulphates, the lead pulp is forced into a large washing apparatus (Fig. 31). This is at

ron tank resting on brickwork, through which is seen the bevelled cog-wheels which drive the agitator C. The motive power is supplied by the engine E. The tank is covered with the wooden dome I, having a manhole and an outlet at the top for the escape of steam. To gain access to the manhole, the tank is provided with a passage G, which is reached by the ladder F. Inside, the lower part of the tank is bevelled to allow the lead sulphate to be more effectually washed, and the whole is covered with lead sheets burnt together and hammered flat to the circle of the tank. Inside also is fixed the wooden supports, which carry the perforated lead steam coils B. The charge in the condenser is pumped in so that the coils are well covered, and the necessary quantity of sulphuric acid then added. On setting in motion the agitator, the contents, aided by the steam blown on, are soon brought into a state of commotion, and to a temperature of 80° C. This is continued for three hours, and results in the conversion of the oxide to sulphate of lead, with the formation of soluble sulphates of zinc and iron.

To free the lead pulp from these foreign bodies and the acidity consequent on an excess of acid used, the contents are allowed to settle, and the supernatant liquor run off from a valve. A fresh supply of water is then added, and the pulp again well agitated; on settling, the clear liquor, as before, is run off. This is repeated until the wash water is free from acidity and the salts of zinc and iron. The pulp is now pumped from the washer, passing through a lead pipe to large presses, whence it is freed from a large portion of the water, the cakes inside the filtering chambers retaining only about 10 per cent.

On removing the plates (see Fig. 32, showing a filter plate with the corrugations and perforated plate covering them), which are mounted on deep rectangular bars, the cakes fall

on to a travelling band which carries them to the drying room, where they are dried in shallow earthen dishes, arranged

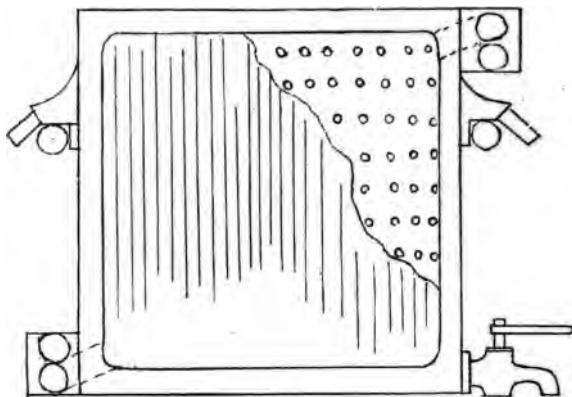


FIG. 32.—Filter-Press.

on racks, the heat being supplied by flues running the length of the room. The finished product is sent out in the dried state or ground with linseed oil.

Two hundred and forty parts of pure galena yield three hundred and four parts of sulphate of lead, the pigment produced being non-poisonous and but slowly affected by sulphuretted hydrogen.

The Pilcher Lead Company (says the *Scientific American*, 1896) obtain lead sulphate as a bye-product in the smelting of non-argentiferous lead ore. It is made in two colours—(1) white, used for all colours incident to the use of ordinary white lead; and (2) blue, which is a preferable colour when used as a pigment for iron, or as a material in the manufacture of rubber. The ore is first smelted with raw coal and slaked lime in a special furnace, using an air blast to obtain the required heat; the hotter the fire, the more lead is volatilised, and the more fume produced.

The products of this smelting are “pig” lead, pasty slags containing more or less lead, zinc, and other constituents of

the ore, and the fume. The latter is drawn off by an exhaust fan, through a settling chamber to a bag house, which contains a large number of woollen bags, for filtering the fume out of the gases. This fume is a lead-coloured, impalpable powder, known as "Blue Powder." It is removed, ignited, and allowed to burn for several hours, which converts it into white, coherent crusts. These crusts, with some oxidised ores and hearth slags, are next charged into a special furnace with a very hot coke fire. The products of this smelting are "pig" lead, slags poor enough in lead to be thrown away, and the fume, which is perfectly white and in a fine state of subdivision, suitable for a white pigment, and is sold as such, or ground in oil.

Made in this manner, it is claimed that the ground pigment does not crack or peel when applied to metallic surfaces, has good covering power, and is unaffected by ammonia or sulphur fumes.

(d) *Sulphite of Lead*.—This pigment has but a very limited use as a lead substitute. It is a white, insoluble powder, which when heated gives off sulphurous acid, and leaves a mixture of sulphate and sulphide of lead. The pigment is prepared by double decomposition, or by passing sulphurous acid into a neutral acetate of lead.

2. *Substitutes used as Pigments, but containing no Lead.*

(a) *Basic Nitrate of Bismuth*.—This product has been used under the name of "Pearl White." It is prepared (1) by heating nitrate of bismuth for some time to 80° C., or (2) by decomposing the acid solution of the nitrate with water, the basic nitrate being precipitated as a white powder.

(b) *Sulphate of Strontium*.—Under the name of "Strontian White" this substitute is known. It is produced by precipitating a soluble strontium salt with sulphuric acid. The

precipitate formed is a white powder, but very slightly soluble in either hot or cold water.

(c) *Oxide and Carbonate of Magnesia*.—Both are known as “Magnesia White.” The oxide is produced as a white amorphous powder when the metal is burnt in air, or when the carbonate is ignited. It is tasteless and inodourless, and but very slightly soluble in water. The carbonate, also found native as magnesite, is prepared by precipitating a soluble magnesium salt with sodium carbonate.

(d) *Tungstate of Barium*.—This product, known as “Tungsten White,” is obtained by dissolving sodium tungstate in water, and precipitating from the solution, as a white powder, the tungstate of barium by the addition of barium chloride.

(e) *Hydrate of Cadmium*.—Under the name of “Cadmium White” this compound has been used. It is prepared by adding potash to a sulphite or chloride of cadmium.

(f) *Antimonious Oxide*.—This oxide, under the name of “White Antimony,” has been put forth as a pigment. Artificially it is produced by heating trisulphide of antimony with strong hydrochloric acid, and pouring the resulting solution into a boiling solution of sodium carbonate, the antimonious oxide being precipitated as a white powder.

(g) *Oxide of Zinc*.—See “Salts of Zinc,” page 166.

(h) *Silicate of Zinc*.— „ „ page 166.

(i) *Sulphide of Zinc*.— „ „ page 164.

(j) *Oxide of Zinc and Barium Sulphate*.—The mixture of these two bodies forms the pigment known as “Charlton White.”

(k) *Barium Sulphate*.—See “White Minerals used as Pigments,” page 176.

(l) *Carbonate of Lime*.—See “White Minerals used as Pigments.”

(m) *Silicate of Alumina (China Clay)*.—See “White Minerals used as Pigments,” page 178.

3. *Substitutes in which the value of the Lead Compound present is lowered by the addition of Oxide of Zinc or of Native or Precipitated Sulphates or Carbonates of Barium, Strontium, Lime, Magnesia, etc.*

(a) Venice white is composed of equal parts of barium sulphate (barytes) and white lead.

(b) Dutch white contains three parts of barium sulphate to one part white lead.

(c) Hannay's white is a mixture of oxide of zinc and chloro-sulphite of lead.

(d) Freeman's white is a mixture of sulphate of lead with zinc oxide and a small proportion of barytes.

(e) Marine white is composed of 75 per cent. of sulphate of lead and 25 per cent. of barytes. Many mixtures of mineral whites, zinc oxide and sulphide, and lead pigments, exist. They are made up to suit the requirements of each manufacturer.

CHAPTER XII.

ZINC AND ITS COMPOUNDS.

Occurrence.—Zinc and its compounds have a wide industrial application. The metal is rarely found in the native state, but in a combined form with sulphur and carbonic acid, as blende and calamine. Other combinations of zinc with silica exist as willemite, an anhydrous silicate of zinc ($2\text{ZnO} \cdot \text{SiO}_2$), found near Aix-la-Chapelle, and as Smithsonite, a hydrous silicate ($2\text{ZnO} \cdot \text{SiO}_2 + \text{H}_2\text{O}$), occurring in fibrous forms in Carinthia. Zinc also is found in union with oxygen, as zincite or red zinc ore, the mineral being found in New Jersey, mixed with a little oxide of manganese.

For metallurgical purposes, blende and calamine are the minerals chiefly used in extracting the metal. They are found in the carboniferous and magnesian limestones in England, France, Spain, and other countries. Blende is generally associated with galena, iron and copper pyrites and heavy spar, the mineral crystallizing in rhombic dodecahedrons, having a highly conchoidal fracture and an adamantine lustre. It is found either transparent or translucent, with a specific gravity of 4. Calamine occurs in concretionary forms and compact masses of a yellowish-white colour when pure, but generally tinged with brown, from the presence of oxide of iron. It crystallizes in the form of rhombohedra, and has a specific gravity of 4.4. The follow-

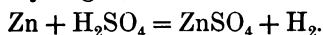
ing analyses are representative of the composition of the two minerals:—

	Blende.			Calamine.	
	(1)	(2)		(3)	(4)
Zinc . . .	55.43	50.24	Zinc oxide . .	54.18	57.19
Lead . . .	4.85	3.79	Ferric oxide . .	8.92	3.60
Iron . . .	2.79	3.18	Alumina . . .	2.84	1.08
Alumina . . .	1.93	4.84	Lime . . .	5.11	2.79
Sulphur . . .	32.77	30.04	Magnesia . . .	2.29	4.38
Silica . . .	2.01	5.22	Carbonic acid .	25.42	29.25
Lime	2.65	Silica . . .	1.10	1.63
	99.78	99.96		99.86	99.92

Properties of the Metal.—Zinc is a bluish-white metal of considerable lustre when newly polished. It melts at 412° C. and boils at 1040° C., giving off a vapour which ignites in contact with air, forming zinc oxide. *In vacuo*, according to Demarcay, the boiling-point of the metal is lowered considerably. The specific gravity varies from 6.86 to 7.21, according to the density, which is increased by hammering. Zinc has a specific heat of 0.094 and a tensile strength of 7.54 tons per sq. inch. At 210° C. the metal becomes so brittle, that it is easily reduced to powder, the particles of which may be made to unite in a concrete mass, by the application of a pressure of 38 tons per sq. inch. Under similar conditions, the particles of lead require, for uniting, a pressure of 13 tons.

Zinc is but little affected by the atmosphere; the thin film of oxide first produced on exposure, does not increase, but forms a coating which protects the metal from any chemical action with atmospheric gases or moisture.

The metal is readily soluble in acids, forming zinc salts with evolution of hydrogen, thus—



It is also soluble in alkaline solutions, forming a soluble compound of zinc and the alkali, and giving off hydrogen gas.

To prepare a chemically pure zinc from spelter, the latter is dissolved in sulphuric acid, and the impurities precipitated by sulphuretted hydrogen. After filtering off the insoluble sulphides, the filtrate is boiled to expel any remaining gas, the zinc being then precipitated as a white carbonate, by means of a solution of carbonate of soda. After washing the precipitate, and re-dissolving it in sulphuric acid, the metal is obtained by electrolysis; or the carbonate, after drying, may be converted by ignition into zinc oxide, which is further reduced to the metal, by distillation with pure charcoal.

In commerce, zinc is known as spelter, the commercial article being always contaminated with small proportions of lead, iron, copper, and tin. Iron gives a certain hardness to the metal, but does not affect its tenacity; on the other hand, the presence of even a half per cent. of lead lowers the retentive property considerably. Copper and arsenic render the metal brittle, and thus more difficult to roll into sheets. Zinc, from its lightness and durability, is used largely for roofing purposes, and in the lining of vessels, tubing, etc.

As a coating for iron sheets, it is used extensively in the "galvanising" process.

Alloys.—Zinc unites with certain metals forming alloys having a great value in the arts, and foremost among these may be placed the compound of zinc and copper, known as brass. In blending these two metals together, some of the most interesting shades of colour are produced, ranging from a reddish-yellow down to a shade approaching the colour of zinc. The former is seen in alloys containing over 80 per cent. of copper, and the latter when the percentage of that metal is less than 25. The percentage of zinc in ordinary

brass castings varies from 27 to 34, according to the purposes for which they are used. For brass wire about $29\frac{1}{4}$ per cent. is used, the metals being alloyed with a little tin and lead.

The following analysis may be taken as a type of the composition of brass wire:—

Zinc	29·26
Copper	70·28
Tin	0·20
Lead	0·26
								100·00

In preparing the alloy for castings or wire, the copper is first melted in large plumbago crucibles, placed in a furnace, and the zinc then added gradually, in pieces, until the whole is melted and alloyed. After removing the crucible from the fire, and skimming the surface to remove the dross, the contents are poured into moulds for subsequent use. For small castings, requiring no great strength, scrap brass is generally melted with a little copper and zinc, to form the alloy. With higher proportions of zinc, copper alloys itself, forming the well-known Muntz metal, Delta metal, Sterro metal, and Aich metal. The two latter are very strong and elastic alloys, with a breaking strain of 85,080 lb. per sq. inch. They are very malleable at a red-heat, and can be hammered, rolled or drawn into wire; they have been used in the manufacture of English and foreign ordnance. Delta metal is very malleable and is used for a variety of purposes, while Muntz metal forms an excellent sheathing for wooden ships.

The following analyses represent their composition (Roberts-Austen):—

IN 100 PARTS.

	Zinc.	Copper.	Iron.	Lead.	Phosphorus.
Muntz metal	40·00	60·00
Delta metal	43·47	55·10	1·08	0·3%	0·10
Sterro metal	41·80	55·33	4·66
Aich metal	38·12	60·00	1·50

tion of this period, the tubes are removed and cleansed of the deposits of zinc fume, which are used in the next charge, the condensed zinc in a liquid form meanwhile being withdrawn from the nozzles by large iron ladles. When emptied, the

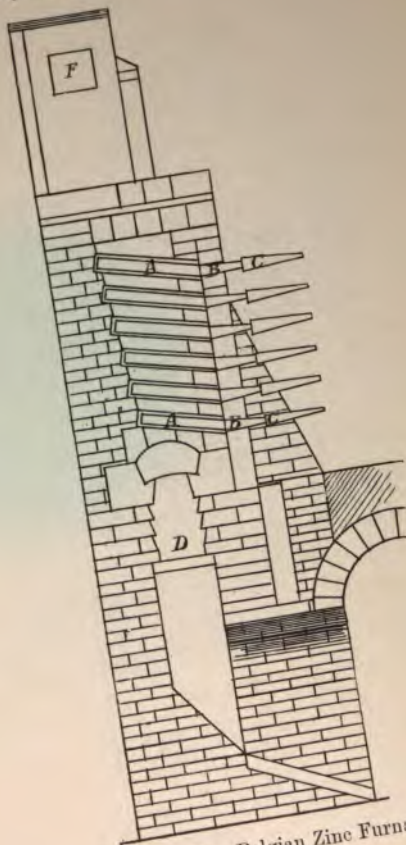


FIG. 35.—Belgian Zinc Furnace.

connections are remade and the distillation continued another two hours, when the same cleansing of the tubes and withdrawing of the molten zinc is repeated. This is continued during the twelve hours necessary to work off the charge. On finishing, the slag, containing 8 to 10 per

zinc, is removed for further treatment, and the recharging with ore and flux commenced. The direct yield of metal from a charge worked by the Belgian process averages 57 to 59 per cent. of the metal in the roasted ore, and each ton yielded requires a coal consumption of about $5\frac{1}{2}$ tons.

The crude metal, which on removal from the nozzles solidifies, requires to be remelted, the zinc and other metallic oxides skimmed off from the surface, and then cast into cakes or ingots, before being brought into commerce.

Silesian Process.—By this process a charge of ore and flux is better worked, and leaves a slag containing less zinc than that removed from the Belgian furnaces, owing to the flat-bottomed arrangement of the muffles used, which enables them to be supported from end to end, and thus able to withstand a higher temperature without collapsing—a result which yields a better distillation.

The ores used are either blende or calamine, and are thoroughly roasted or calcined in a reverberatory furnace for

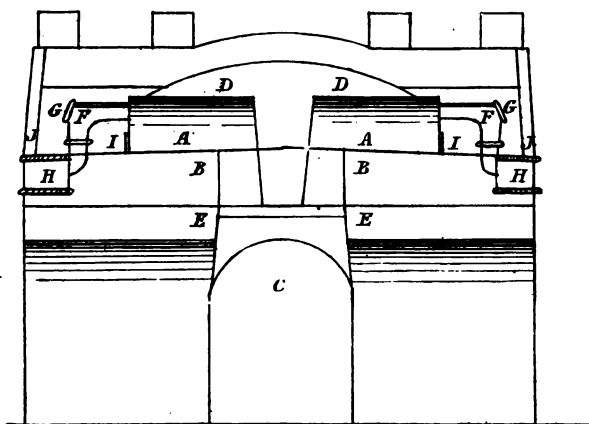


FIG. 36.—Silesian Furnace. Section.

twenty-four hours before smelting. In Fig. 36 a section is shown of the Silesian furnace. It is built of good fire-bricks,

and in a form nearly square, the sides being well clamped with rods. Generally, twenty-four muffles are arranged in each furnace, forming two rows of twelve muffles each, A A, which rest on brick platforms B B, slightly sloping from the centre, the whole being heated by a central fire-place C, running two-thirds of the furnace length. The muffles are moulded from good fire-clay, and then carefully annealed before using. They are D shaped, with a length of 3 ft., a width of 10 in., and a height of 16 in. In working, the muffles are arranged in pairs, each pair being partly enclosed in a rectangular and arched compartment D D, formed of bricks and tiles, and their closed ends are placed nearest the fire. The main flues E E run under the bed of the furnace, and to which they are connected by suitable openings in the brick-work. After circulating round and thus heating the sides and top of each muffle, the spent gases by their downward passage also heat the under part, and thus a more complete distillation is effected than if the gases were carried off from the roof of each compartment. For condensing the zinc vapours, the muffles are provided with curved fire-clay tubes F F, having movable plates G G, and to which are attached cast-iron tubes for conveying the products of distillation, in the form of metallic zinc or any zinc oxide, mechanically carried over, to the chambers H H, below the furnace level. The residual matter in the muffles is raked through the openings I I, and the charging is carried on by removing the plates G G. In working, the front of each compartment is closed by a sheet-iron door J J, provided with an opening for observing the temperature of the furnace.

A charge for each muffle runs about 95 lb., and consists of two-thirds calcined ore and zinc skimmings mixed with one-third finely powdered bituminous coal, and the working off of the charge is similar to that of the Belgian furnace.

By either of the above processes, the direct yield of the

aced in each retort, through the nozzle, by means of a
pop, and in a short time the blue flame of carbonic oxide is
en burning from the mouth. On this changing after a

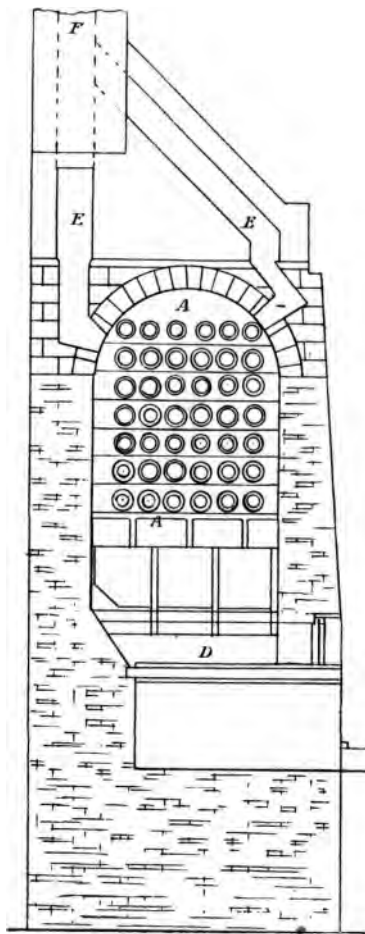
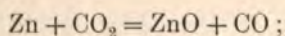


FIG. 34.—Belgian Zinc Furnace.

time to greenish-white—an indication that zinc vapours are
distilling over—the sheet-iron tubes (C C) are affixed, and the
distillation allowed to proceed for two hours. At the expira-

Fry (English patent, 1898) prefers to convert the whole of the zinc in the residues into oxide, as a more economical way of treatment. For this purpose they are mixed with 10 to 20 per cent. powdered coal, and then charged into a Siemens regenerative gas furnace, the hearth or bottom being composed of a neutral or basic material capable of withstanding the action of basic slag. The gas and air ports of the furnace, and also the valves, regenerators, flues, etc., are of a specially large size, in order to prevent choking, and to deal with the increased volume of fumes, over and above that from the combustion of the gases produced from the coal used for heating purposes. The charge is melted down at a temperature of 2000° to 2500° F. ($= 1093^{\circ}$ to 1371° C.), the bulk of the zinc being eliminated during the melting period, passing off in the form of white oxide, and condensed in large chambers. After the charge has become molten, it is well stirred, to promote the separation of the last portions of zinc, the end being seen in the cessation of the dense fumes of zinc oxide. The condensed oxide can either be used as a pigment, or may be reduced to metallic zinc.

The costly and complicated methods of zinc extraction have been an inducement to metallurgists to devise a more economical process, whereby the direct yield of the metal may be increased, with a reduction in the heavy outlay for labour and fuel. Their labours have been mainly centred in the application of the blast furnace for the treatment of zinc ores; but the results have not up to the present been a commercial success. The difficulty in using the blast furnace is due to the presence of carbonic acid in the gases of combustion, which, coming into contact with the volatilised zinc vapours, reproduces the zinc oxide, passing as such into the condensers, thus—



and so powerful is this action, that, according to the researches

of Lencauchez, the presence of even a half per cent. of carbonic acid in the products of combustion would be sufficient to oxidise the metal.

If it were possible to burn the fuel in the blast furnace into carbonate oxide, by withholding a portion of the oxygen in the blast, or if it were feasible, by any other means, to provide an atmosphere of this gas in the furnace, the problem would be solved, for carbonic oxide has no action on zinc vapours at a high temperature, which consequently would pass over unoxidised.

Steger (English patent, 1888) considers that this end can be attained by heating the blast up to 1200°C ., when only a trace of carbonic acid is formed with the carbonic oxide. He recommends the blast furnace to be horizontal instead of vertical, the charge of ore and fuel being made from a hopper above, and the whole brought to a full red heat by a blast heated to 1200°C . Reduction then ensues in an atmosphere of carbonic oxide, the metallic vapours being unaffected.

Walsh (English patent, 1889) converts the carbonic acid in the combustion gases into carbonic oxide, by passing them over carbon heated in a separate chamber to a temperature of 1400° to 1500°F . ($= 760^{\circ}$ to 815°C .), and the zinc vapours, being unchanged by the latter gas, pass over into a condenser built of two parallel and horizontal pipes, joined together by vertical tubes, the condenser being kept at a temperature a little above the melting-point of zinc.

Clere (English patent, 1889) again uses a cold mixture of the roasted ore and charcoal, impinging on the mixture a blast having a temperature nearly equal to the melting-point of iron. This action volatilises the zinc in an atmosphere of carbonic oxide, the vapours of the metal condensing as a fine dust.

The complex sulphide ores of the Broken Hill type, are

treated by Swinburne and Ashcroft (English patent, 1899) by heating in a converter a mixture of crushed ore and fused zinc chloride, in the form of a cream. At the bottom of the converter is connected a pipe, through which chlorine gas is driven into the mass, the gas being rapidly absorbed by the metals, with evolution of sulphurous acid. The temperature is now raised so as to volatilise the formed zinc chloride, which is condensed and treated for the metal.

Ellershausen (English patent, 1900) first subjects the raw ore to a metallurgical treatment, and afterwards separates the zinc electrolytically from a solution of the fume. He smelts the ore in a blast furnace, using lime as a flux, the fume and gases emitted therefrom being forced by a fan under a layer of water in a condenser. The sulphurous acid acting with the water dissolves out the zinc oxide, and from this solution the metal is recovered by electrolysis.

Wet Methods of Zinc Extraction.

Great attention has been paid by metallurgists to profitably using a wet method (either by precipitation or electrolysis) for treating zinc ores, and more especially that class known as mixed sulphides, containing 10 to 20 per cent. of the metal, along with varying proportions of copper, iron, and lead sulphides, whose treatment constitute one of the most intricate problems connected with the metallurgy of zinc.

By Precipitation.—At Leadville, U.S.A., the precipitation method is carried out on complex ores, by roasting them to sulphates, and, after lixiviation with boiling water to dissolve out the soluble salts, the filtered solution is treated with lime to precipitate the zinc as oxide, which is subsequently dried and then distilled with powdered coal to recover the metal.

Maxwell Lyte (English patent, 1887), after calcining the ore, treats it with hot dilute hydrochloric acid, which forms chlorides with all the metals present. On cooling, the

chloride crystallizes out, leaving a supernatant liquor containing the soluble chlorides of iron, copper, and zinc; the first is separated by treating the solution with limestone, which precipitates the iron as carbonate; on filtering and adding scrap iron, the copper salt is reduced to the metal, which deposits itself on the iron, while the zinc is removed as oxide, on treating the solution further with calcium hydrate. On drying and mixing the zinc oxide with carbonaceous matter, the metal is obtained by distillation.

It has been proposed to treat zinc ores by means of polysulphates of the alkalies. Finding that sulphuric acid is the active reagent in this action, Abel (English patent, 1899) treats the ore direct with the acid. The crushed ore is placed in a pan heated from below, and which is arranged in connection with a muffle furnace. On adding the acid, the sulphur is converted into sulphurous acid, which passes off together with the muffle gases. The mass remains in the pan until it has assumed a pasty condition, whereupon it is pushed over into the muffle, spread out, and then allowed to remain with frequent stirring until the development of gas ceases. The melt is now lixiviated with water, which dissolves out the soluble zinc sulphate along with other soluble sulphates, and, from the clear solution, the zinc is precipitated as oxide. In the gangue, the whole of the lead is found as sulphate, and is treated metallurgically, for recovery of the metal.

Davis Brothers, in their treatment of zinc ores, more especially those of the type of mixed sulphides, propose the use of nitric acid as a solvent (English patent, 1900). The operation is carried on in stone or earthenware vessels, provision being made for charging, and discharging and for heating and agitating, the contents of each vessel. On heating, the crushed ore is rapidly attacked by the nitric acid, which dissolves most of the metallic constituents as

nitrates, leaving an undissolved residue of silica, sulphur, and lead sulphate. Any gold and silver are also found in the residue, and, to ensure the complete precipitation of the latter, a small quantity of hydrochloric acid is added during the solution of the ore. The contents from each vessel are now discharged, and the solid residue separated and washed. In the solution a portion of the lead exists as nitrate, along with the nitrates of zinc and iron, and to it is added oxide of zinc, which precipitates the iron as hydrate, and other impurities, behaving in the same manner towards oxide of zinc. After separation of the iron precipitate, the solution is treated with a further quantity of oxide of zinc, and, while still warm, carbonic acid is blown through it. This affects the separation of the lead as carbonate, and the added zinc oxide goes into solution, which is now practically a solution of nitrate of zinc. After concentration to a specific gravity of 1.5, the liquor is run into a suitable furnace, and heated to dryness, the zinc nitrate being converted to zinc oxide, which remains behind. The gaseous products drawn away, are collected for oxidation and recovery of the nitric acid, to be used again. In the solid residue resulting from the treatment of the ore, are found the lead, silver, and gold, and is specially treated for the recovery of these metals.

By Electrolysis.—With the advent of less costly appliances and the discovery of a cheaper source of electrical power, the commercial development of the many efforts made to profitably extract zinc from its solution, by electrolysis, will be assured. Before applying the electrical force, the zinc in the ore requires to be brought to a form by which it becomes soluble in water, and, for this purpose, Cassel and Kjellin roasted a Swedish blende to produce a maximum yield of zinc sulphate, which, being soluble, was washed out of the roasted mass.

The electrolysing vessel used for the decomposition of the zinc salt has a porous partition; and around an iron anode, is placed a solution of iron sulphate, while the solution of the zinc salt surrounds the cathode. On passing the current through, metallic zinc is deposited from the latter solution, while its equivalent quantity of sulphuric acid is separated at the iron anode and dissolves it to sulphate. The electromotive force of decomposition, under the circumstances, is the difference between that required to decompose the zinc sulphate, and that of the iron sulphate, or about $\frac{1}{3}$ rd of a volt, thus allowing for the separation of the zinc without decomposing the water of the solution.

Heinzerling (English patent, 1898) roasts the zinc ores completely to oxide, which is dissolved in a concentrated solution of magnesium chloride. This solution is then electrolysed, the zinc separating out, while the dissolving agent can be used over again. For decomposition a current of 200 amperes per square metre is used, the solution during the passage being kept at a low temperature.

Cowper-Coles (English patent, 1898) in his process of treating mixed sulphides, first crushes the ore and then sieves it through a fine mesh; it is then roasted so as to convert the sulphides present, into sulphates and oxides. The roasted mass is afterwards placed in a reciprocating or revolving screen, the fine dust being withdrawn by the exhaust of a centrifugal fan, directly into the leaching vat, containing a weak solution of sulphuric acid (1 oz. sulphuric acid to 1 gallon water), which dissolves out the metal or metals as sulphates. The remainder in the screen is placed in a second leaching vat, having a false bottom covered with filtering cloth, and treated with a weak solution of the acid, which combines with the zinc and copper to form sulphates. The clear solution is drawn off from beneath the vat, and added to that from the leaching of the dust from the screen,

the whole being passed through a body or bed of iron and carbon, on which the copper is deposited in the metallic state, and may be recovered as a fine powder, by washing. After the zinc sulphate solution is freed from the copper, it is then passed through the electrolysing cells, through which the electrolyte is circulated. In these cells are vertically revolving cast-iron discs, serving as cathodes; lead plates being employed for the anodes. The iron discs are slowly rotated, and are provided with fillets of wood, which can be detached to allow of the removal of the deposited zinc in the form of segments, when the metal has attained the highest degree of thickness. The current density employed varies from 15 to 20 amperes; a convenient voltage at the terminals of the electric generator being from 100 to 150 volts, the voltage at the terminals of the cells varying from 1 to 2 volts.

The lead remaining in the residue is leached out by means of a solution of caustic soda, and from the clear solution the metal can be recovered by precipitation. After the caustic soda solution has been used a number of times for leaching out the lead, it becomes partly converted into silicate; on adding lime, however, to the solution, caustic soda is again formed.

The silver and gold present in the residue after removal of the lead are extracted by a weak solution of potassium cyanide, and further treated for the recovery of the precious metals.

Professor Richards (1895), experimenting on a method of refining very impure spelter, says that a metal of unexceptional purity can be obtained by dissolving the impure spelter in a bath of sulphuric acid, and using an electrical current of 100 amperes per square metre at 1.3 volts tension, keeping the solution well agitated by suitable mechanical means. He prevents the accumulation of iron in

the solution by blowing air through it continually, which oxidises and precipitates the iron as basic sulphate, which can be separated by filtration.

Flue Dust.

In the roasting of sulphide ores, a considerable accumulation of fine dust consisting of sulphides and sulphates of zinc, lead, silver, etc., and, on removal, it is generally mixed with a charge of roasted ore and smelted.

Threlfall (English patent, 1898) treats the dust with a solution of acid sodium sulphate, which dissolves out the zinc as sulphate, leaving the lead and silver unaffected. From the solution, the metal is recovered by precipitation, as oxide, and then reduction with carbonaceous matter in a retort or muffle, or by electrolysis, while the residue can be treated by a dry or wet method to obtain the lead and silver.

Sheet Zinc.

Since the discovery that zinc, when heated from 100° C. to 130° C., loses its brittleness, and becomes malleable, and thus capable of being rolled into sheets, a great impetus has been given to its use in roofing, guttering, and for cisterns, baths, and other purposes, owing to its lightness and durability when exposed to air and moisture. For although sheets of zinc so exposed, quickly absorb oxygen and carbonic acid, the film of oxide and carbonate so produced, acts like an anti-corrosive paint, in preventing any further corrosion of the metal beneath.

In preparing the spelter for rolling, it is necessary to bring down the lead present to not more than a half per cent.: for this purpose, the ingots are melted on the hearth of a reverberatory furnace, and the lead separated by liquation. The molten zinc is cast into ingots, which are subsequently heated by the waste gases of the reverberatory furnace to a

temperature not above 130°C ., and are then passed through a rolling mill to the thinness required. On cooling, the rolled sheet retains its malleability. At a temperature of 200°C . the metal becomes so brittle, that it may be reduced to a fine powder by pounding in a mortar, and in this form has been used as a metallic paint for protecting iron. The zinc pigment known as "grey oxide" is practically the metal in a very fine state of division.

Salts of Zinc.

In addition to the native sulphide and carbonate, used metallurgically, the metal unites with other elements forming the chloride (ZnCl_2), selenide (ZnSe), telluride (ZnTe), cyanide ($\text{Zn}(\text{CN})_2$), bromide (ZnBr_2), oxide (ZnO), sulphate (ZnSO_4), silicate (Zn_2SiO_4), and chromate (ZnCrO_4).

Zinc also forms, artificially, a white sulphide, by precipitation with an alkaline sulphide, and double salts in conjunction with cobaltic, nitrate or chloride and ammonium chloride.

Of these compounds, only the double salts, chromate, sulphate, chloride, artificial sulphide, silicate, and oxide, have any practical use in the arts.

Zinc-cobaltic Protoxide.—This compound is known as a green pigment, under the names of zinc green and Rinmann's green. It is prepared by precipitating a solution of cobaltic chloride, containing 10 per cent. of the salt, with sodium phosphate, well washing the precipitate formed, and then mixing it with about three times its weight of zinc white (ZnO).

After drying in a stove, the mixture is calcined.

Wagner gives the composition of a zinc green, made in this manner, as follows:—

Zinc oxide	71.68
Phosphoric oxide	8.29
Cobaltic protoxide	18.93
	<hr/>
	99.90

Another method, but less satisfactory, is by precipitating a mixture of zinc sulphate and cobaltic nitrate, with sodium carbonate, and, after well washing, the green precipitate formed is calcined. The green pigment prepared in this way, is known as Rinmann's green.

Ammonio-chloride of Zinc.—This double salt is formed by dissolving sixty-eight parts of zinc chloride and fifty-four parts of ammonium chloride in water, and then evaporating to the crystallizing point. Owing to its power of dissolving oxides of copper and iron, it is used largely in "tinning" or "zincing" these metals.

Zinc Chromate.—Known as zinc yellow or buttercup yellow, this compound forms a beautiful and stable yellow pigment. It is produced by dissolving zinc sulphate in hot water, and then adding a solution of potassium chromate. The yellow precipitate when washed and dried has the following composition, according to Wagner:—

Chromic oxide	14·94
Zinc oxide	75·35
Carbonic acid	3·61
Water	6·19
	<hr/>
	100·09

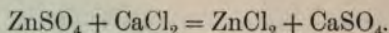
Zinc Sulphate.—The "white vitriol" of commerce is a sulphate of zinc, having the composition, when pure, of—

Zinc sulphate	56·09
Water of crystallization	43·91
	<hr/>
	100·00

On the large scale, it is made by roasting zinc blende completely to zinc sulphate, in a reverberatory furnace, and then lixiviating the mass in water to dissolve out the soluble salt. After filtration, the liquor is evaporated down, when

the salt crystallizes out in the form of rhombic prisms. Zinc sulphate is used not only in dyeing and calico-printing, but also in the manufacture of varnishes and drying oils for painting.

Zinc Chloride.—In the anhydrous state, this compound is a greyish wax-like substance, to which the name of “butter of zinc” was given by Hellot, who prepared it by distilling zinc oxide with ammonium chloride. Pott also, obtained the same body, by distilling zinc with corrosive sublimate, and Persoz, by heating dehydrated zinc sulphate, with calcium chloride, thus—



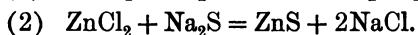
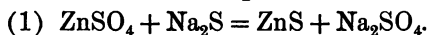
For commercial purposes, it is made by dissolving scrap zinc in hydrochloric acid, in large stone or wooden cisterns, provided with a steam coil. On heating to 50°C ., the zinc is rapidly dissolved, and then a small quantity of bleaching powder added to precipitate the iron present, and the liquor is then allowed to settle.

The clear zinc chloride solution, after syphoning off, is boiled down in enamelled iron pots, a little potassium chlorate being added to oxidise any organic matter, and also some pure hydrochloric acid to dissolve any basic salt formed. On solidifying, it is packed, while still warm, in iron drums for the market.

A solution of zinc chloride is a powerful disinfectant and deodourant. For preserving timber, Sir William Burnett patented its use, in the proportion of 1 lb. of salt to 5 gallons of water. It is also well known as an agent for weighting cotton goods. When zinc chloride solution of 1.7 specific gravity is mixed with excess of zinc oxide, a very durable pigment, known as zinc oxychloride, $\text{ZnCl}_2 \cdot 3\text{ZnO} \cdot 4\text{H}_2\text{O}$, is formed, which is unaffected by sulphuretted hydrogen gas.

Artificial Zinc Sulphide. — This product, known as

lithophone, is a white pigment, produced by adding sodium sulphide to a solution of zinc sulphate or chloride, thus—



On washing out the soluble soda salts, the precipitate remains as a white amorphous powder, soluble in dilute mineral acids, but insoluble in acetic acid.

The composition is as follows:—

Zinc	67·01
Sulphur	32·99
									<hr/> 100·00

On a large scale, it is prepared by taking sodium sulphate or salt cake, and mixing it with half its weight of bituminous coal, the mixture being fluxed in the ordinary black ash furnace, till yellow fumes are developed. The resulting cakes of black sodium sulphide are porous, and easily lixiviated in tanks provided with steam pipes, and heated to about 200° F., so as to get a strength of 25° Twaddell. On settling, the clear liquor, which consists principally of sodium sulphide mixed with some sodium bisulphide and carbonate, but free from iron, is treated with a solution of zinc sulphate or chloride, until hydrated zinc sulphide, mixed with some free sulphur, is precipitated, and towards the end of the operation a small proportion of zinc carbonate also falls down. The precipitate is thoroughly washed, dried, and then ignited in gas retorts or muffles, till the bluish-yellow flame due to the sulphur disappears, when the product is withdrawn into water, forming a white powder, which, on drying, forms the pigment of commerce. Zinc sulphide is a very white compound, but possesses little covering power. It is used alone, or sometimes with zinc oxide. The patent "zinc white" of Griffith's, is a zinc sulphide, formed by precipitating the sulphide from the sulphate, by means of a soluble sulphide,

then washing, drying, and calcining the white precipitate, after which it is levigated, ground, and dried for packing, or mixed with oil. Zinc sulphide also enters into the composition of the well-known brands "Charlton white" and "Duresco," the two being a mixture of zinc sulphide with barium and strontium sulphates.

Zinc Silicate.—This compound of zinc is used as a pigment in conjunction with the oxide and sulphide. It is a very white product, but has no body. On a large scale, it is prepared by dissolving water-glass in hot water, and adding a solution of zinc sulphate. The precipitate is then washed and dried.

Zinc Oxide.—Zinc, when heated to a temperature slightly above its melting-point, burns with a bluish-white flame,

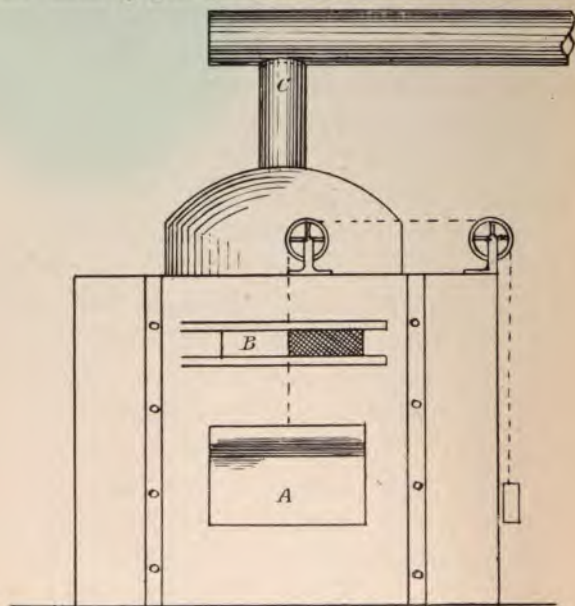
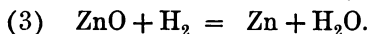
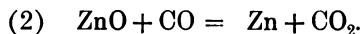
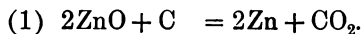


FIG. 37.—Oxidising Furnace.

forming a dense white smoke, which, on condensation, yields a white amorphous powder, known as "flowers of zinc"; this

oxide is decomposed by carbon, carbonic oxide, or hydrogen, with the formation of metallic zinc, thus—



Zinc oxide is readily soluble in mineral acids, and with boracic acid it forms a readily fusible compound. It is the most important pigment of the zinc compounds, and is prepared on a large scale by burning zinc to a vapour, which, on coming in contact with a current of air, is oxidised to a white powder. The oxidising furnace is a brick structure, lined internally with fire-bricks and well tied together with tie-rods. Fig. 37 is an elevation, A representing the charging

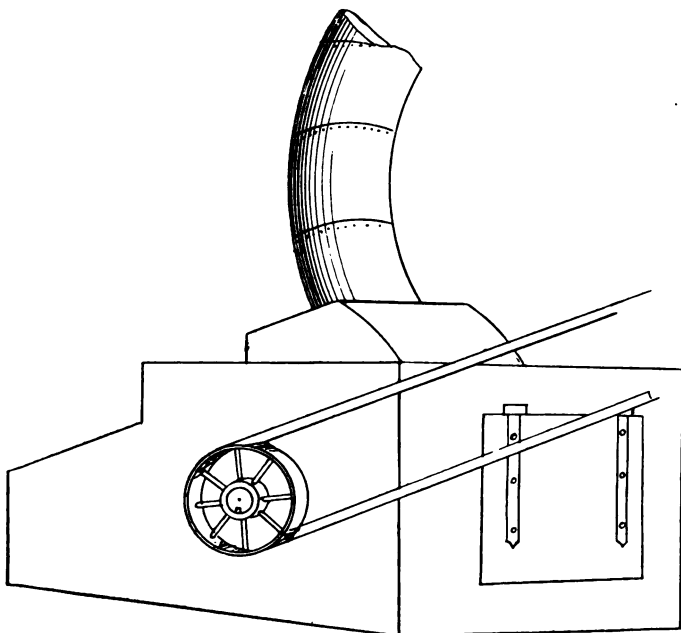


FIG. 38.—Blower.

door, B an upper sliding door, and C the chimney for carrying off the zinc oxide vapours. At the back of the furnace are

placed the tuyeres for supplying the blast to the furnace. On the charge melting and then volatilising, white vapours of zinc oxide rapidly form, and are drawn through the chimney to a main pipe some 3 ft. in diameter, which is connected at one end with a powerful blower (Fig. 38). From thence they are forced through a second pipe of similar diameter to a lofty chamber called the bag-room; the pipe being carried the length of the building and suspended from the rafters. Some 4 ft. apart, and connected by nipples to the pipe, a number of muslin bags, 30 ft. long and 1 ft. wide, are suspended (A, Fig. 39); these, again, are connected with a large bag (B) running horizontally the length of the building, and underneath this are fixed a number of "teats" or bags (C) for collecting the white oxide. At the end of each charge, of which there are six daily, the blower is stopped, and the bags, previously blown out with the pressure, collapse, and are then well shaken, causing the zinc oxide to settle down into the "teats," which are removed, emptied of their contents, and then made ready for the next charge. The white pigment is now passed through revolving sieves of a very fine mesh, to remove any gritty matter, and then packed for the market.

As described above, the manufacture of zinc oxide requires the reduction of the ore to the metal in the first instance, and then the reoxidation of the metal to zinc oxide, before the white pigment is obtained. In carrying out these processes, the erection of a costly plant, along with a subsequent heavy outlay in coal, labour, and repairs, is necessary to accomplish the work.

Many attempts have been made to simplify the procedure by dispensing entirely with the reduction to the metal, and obtaining the pigment direct from the ore, but hitherto with little success, owing to the want of brilliancy produced.

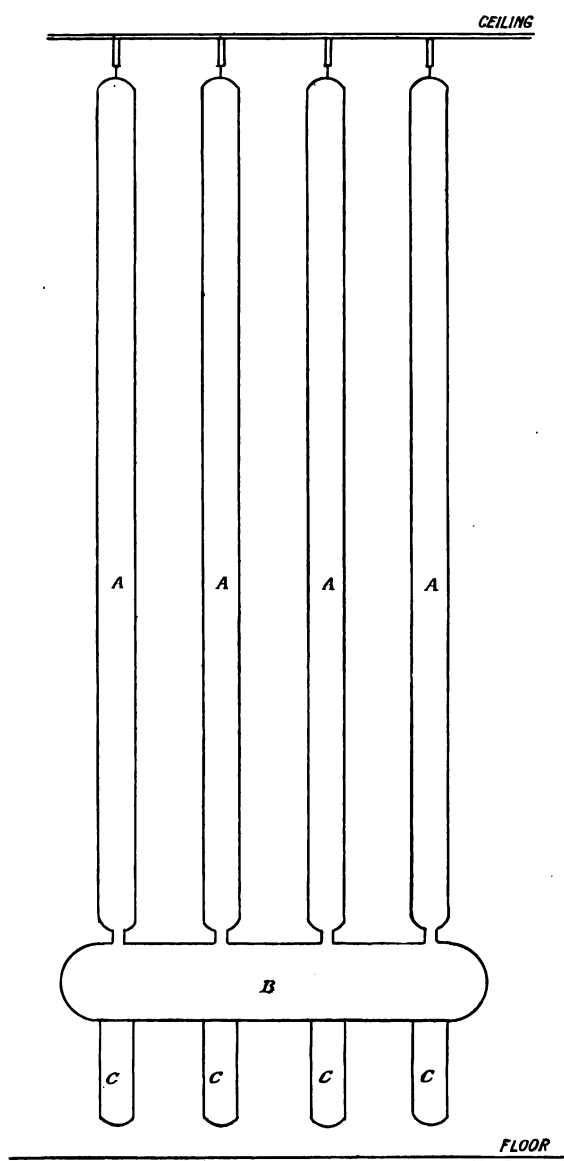


FIG. 39.—Bag-room. Section.

Mr. George Darlington, who has devoted much time to the production of a good white by the direct process, says that a marketable zinc oxide can be made by burning the ore in a furnace, constructed similar to the ordinary coke oven, the crown being semicircular and built of 9 in. brickwork. The bed of the furnace is slightly rectangular, and comprises the bed proper, along with a fire-place, the two occupying an area of 30 sq. ft. The bed proper is a grate of perforated iron bars or plates lying over a closed ashpit, in which the air is forced by a fan-blast. In the crown, there is an opening through which the zinc oxide, as well as the products of combustion from the fuel used in the furnace, are conveyed away into the cooling flues, and from thence pass into the bag-collecting rooms. The furnace is provided with only one door, 2 ft. long and 18 in. high, which serves for charging both the fuel and the ore.

For the production of a white pigment direct from the ore, Rigg (English patent, 1898) roasts the ore completely to oxide; the roasted mass is leached with a solution of ammonium carbonate, or a mixture of ammonium carbonate and ammonium hydrate, which dissolves out the zinc. After allowing the insoluble matter to subside, the clear liquor is treated with a small proportion of hydrated oxide of tin, which precipitates any iron present; on filtering, any copper present in the filtrate, is removed by deposition on zinc plates placed in the liquor. On removal of the copper, the liquor is treated to a current of carbonic acid, which precipitates the zinc as carbonate, and from this the pure oxide is obtained by heating the precipitate.

Zinc white, also called Chinese white, is much inferior to Dutch white lead, as regards body and covering power; the balance in favour of the latter is as 11 to 7, or, as painters express it, three coats of white lead are equal to five coats zinc white. It saponifies with linseed oil, forming a true soap of

zinc, but this compound has a tendency to wash off from exposed surfaces, covered with it. When used, however, in conjunction with white lead, it is found eminently useful, from its superior whiteness and delicacy, for all inside work. For this purpose, the ground is laid on with white lead, and the surface is then produced in zinc white, which yields a richness and beauty one cannot fail to admire.

The drying qualities of zinc oxide vary according to the care in its manufacture, but even the best grades show an inferiority when compared with white lead. This deficiency is due to the excessive fineness and crystalline character of its particles.

When zinc oxide is prepared at a low temperature, its crystalline texture undergoes a partial change, and it is then found that the drying qualities of the pigment have increased; on the other hand, when produced at a temperature considerably higher than the boiling-point of zinc, the crystalline nature is developed, and consequently the drying power of the pigment diminishes. Zinc oxide enters into the composition of all mixed paints, and, when ground with double its weight of red lead in linseed oil, it forms an effective anti-corrosive and anti-fouling paint.

In the production of the pigment, 85 per cent. of the produce is used directly in the manufacture of paints, and the remaining 15 per cent. in the floor-cloth, wall-paper, rubber, earthenware, etc., industries.

The following "mixings" show the proportion of zinc oxide used in some paints:—

No. 1 Mixing.

250 lb. corroded lead (Dutch white lead),
170 ,, zinc oxide,
14½ gallons linseed oil.

No. 2 Mixing.

60 lb. lead sulphate,
60 „ zinc oxide,
380 „ barytes,
16 gallons linseed oil.

No. 3 Mixing.

100 lb. corroded lead (Dutch white lead),
300 „ lead sulphate,
100 „ zinc oxide,
14 gallons linseed oil.

When ground alone, zinc oxide requires 22 per cent. by weight of oil.

As a siccative for zinc white, linseed oil boiled with litharge would not be suitable, owing to the latter blackening in presence of sulphuretted hydrogen. For this reason, other substances are used, as borate, acetate, and sulphate of manganese, sulphate of zinc, etc.

The following are some siccatives in use:—

(1) Mix together 10 parts each of acetate of manganese, sulphate of manganese, and sulphate of zinc, with $14\frac{3}{4}$ parts zinc white. In using, add 2 to 3 per cent. of the siccative to the zinc white oil paint.

(2) Sirel's siccative is made by intimately mixing manganese subchloride with 19 per cent. of zinc white or barium sulphate, 2 per cent. of this mixture being added to the zinc white paint.

Zinc oxide is used in preparing the composition known as white ink, used for writing on dark-coloured paper, the ink being made by saturating zinc white with water and adding mucilage of acacia to thicken the mixture. Before using, the ink requires to be shaken, as the pigment partially settles to the bottom on standing.

Zinc oxide is also used in the preparation of some anti-fouling and anti-corrosive compositions, as seen in the following recipes:—

1. *Anti-fouling Composition.*

Zinc oxide	112 lb.		
Zinc sulphide	28 „		
Barytes	28 „		
Boiled linseed oil foots	4 „		
Naphtha	120 „	} A	} B.
Rosin	128 „		
Gum	10 „		
Calomel	47 „		

A and *B* are varnishes ;

A being a mixture of naphtha and rosin,

B „ „ „ with gum.

In working, the whole ingredients are mixed together, and then passed through the stones.

2. *Anti-corrosive Composition.*

The same ingredients as above, excepting the use of calomel.

From a sanitary standpoint, the use of zinc oxide as a paint is to be commended. It is, unlike white lead, non-poisonous, and, when taken internally, even in considerable doses, produces no greater inconvenience than an irritation of the throat and nostrils, and, after a time, a slight soreness in the joints.

CHAPTER XIII.

PUMICE-STONE—CHINA-CLAY.

ALL painters know the value of good pumice-stone; a description, therefore, of its occurrence and method of preparation for the market will not be inappropriate. Pumice, chemically, is a silicate of alumina, potash, and soda, with minor proportions of lime and oxide of iron. The following analysis represents the composition of a good sample:—

Silica	73·70
Alumina	12·27
Potash	4·73
Soda	4·52
Ferric oxide	2·31
Lime, water, etc.	2·47
	<hr/>
	100·00

Pumice is a lava, rendered light and scoriaceous by the escape of gases, and is found principally in the island of Lipari, Italy. Most of the volcanoes of Lipari have ejected pumaceous rocks at some period or other, but the best stone, according to Mr. N. Douglass, in his Report to the Foreign Office, is the product of Monte Chirica, with its accessory craters, Monte Pelato and Forgia Vecchia, situated in the north-west of the island. These deposits (Mr. Douglass says) cover an area of 3 square miles, and in some instances have a thickness of 5 yards, the pumice being excavated by means of tunnels or galleries dug into the layers of

volcanic ashes that have gradually covered the stone, which is brought to the surface in large blocks or in baskets, and thence sent to the town of Lipari, where it is stored by the merchants in sheds to get thoroughly dry, which not only reduces the weight, but also enables an estimate to be made of the quality. The blocks, weighing 15 lb. and upwards, are separated, and allowed to crumble into so-called "lesconi," and then all is sorted according to its size into (1) large (*grosse*), (2) medium (*correnti*), and (3) small (*pezzame*). The quality is primarily a matter of texture. As pumice is used for polishing purposes, an essential condition is homogeneity of structure and freedom from included crystals; the stone must not be too brittle or too hard, and it is in these respects that the Lipari pumice surpasses that of other volcanic regions.

After it has been divided according to its size, the large stones, known as "*grosse*," are again sorted into three superior qualities, called (1) *flore*, (2) *quasi-flore*, and (3) *mordenti*. These are never filed. After they have been selected, the remainder of the "*grosse*" are filed by hand in order to remove asperities of surface and to see whether the stone is not too friable for use. They are then re-classed into firsts, seconds, and thirds, and designated respectively, "*bianche*," "*dubbrose*," and "*nere*."

In the first classification of the stone, the medium or "*correnti*" quality of stone is exported without further sorting, while the small or "*pezzame*" quality is usually ground to a powder of more than ten different degrees of fineness, according to the work for which it is required.

Besides these, there is an entirely different variety called "*alessandrina*," which is cut with hatchets into brick-shaped pieces and used for smoothing oilcloth, and also a dark heavy stone, which is trimmed and known as "*bastardone*."

The annual production is about 18,000 tons, and the

workmen employed being about a thousand in number, of whom six hundred are miners. In the factories of Lipari, over three hundred workpeople, a large proportion being females, are engaged in sorting and cleaning for the market, the raw pumice-stone from the mines. The price ranges from £2 to £12 per ton, but very fine qualities will bring from £60 to £70 per ton.

White Minerals used as Pigments.

For cheapness solely, certain minerals, more or less of a white colour, such as barytes, china-clay, prepared English chalk in the form of whiting, and Paris white, silica, and ground marble, are largely used, in a finely divided condition, in the mixings of the paint manufacturer. They possess no covering power when ground with oil, and do not add any durability to the paint produced.

Barytes.—This product, known also as permanent white and heavy spar, is chemically a sulphate of barium. It is found in a crystalline form in the cracks and fissures of the lead-bearing rocks of Derbyshire, Flintshire, Cumberland, and Yorkshire in England, and in Germany, Belgium, Spain, and other countries. The raw material when mined is found frequently stained with oxide of iron, and thus requires to be bleached before drying and grinding for the market. For this purpose, the barytes is crushed to a coarse powder, and treated with dilute sulphuric acid in lead-lined vats, the contents being brought to the boil by steam passing through an inside perforated coil. The acid dissolves out the whole of the oxide of iron, leaving a white barytes, which, after washing, is removed to the drying floors, to be dried preparatory to grinding.

When the mineral is free from any discolouring oxide, the bleaching process is omitted, the barytes being simply washed and picked to remove any rock, and then dried on

a tiled floor, heated by flues underneath (see "China-Clay"). The dried product is then crushed to a coarse powder by rollers, and thence carried by an endless band to a double set of millstones, the final passage through, yielding a powder of great fineness, and ready for the market. Having little opacity, barytes cannot be used by itself, but only when mixed with white lead, and, when added to the latter, it must be regarded as an adulteration. Several mixtures of barytes and white lead are manufactured and known in commerce as—

Venice White	.	{ 1 part barytes, 1 part white lead.
Hamburg White	.	{ 2 parts barytes, 1 part zinc white.
Dutch White	.	{ 3 parts barytes, 1 part white lead.

Barytes is also employed in the manufacture of jasperware, and for the formation of white figures, etc., on coloured jars and vessels.

China-Clay.—Washed china-clay or kaolin is used as a cheapfilling in the fabrication of many white and coloured paints.

Chemically, it is a hydrated silicate of alumina with small proportions of lime, magnesia, and alkaline bases.

The qualities inseparable from a good china-clay are whiteness and freedom from grit and dirt, which are obtained by a careful process of levigation from the raw deposits found in deep-seated fissures, extending in some cases to over 100 yards wide, and from $\frac{1}{4}$ to $\frac{1}{2}$ mile in length, in Devon and Cornwall.

These deposits were formerly granite which has undergone decomposition by atmospheric and chemical changes, yielding quartz, mica, and kaolin, and it is the latter, after being freed from the extraneous quartz, mica, and any undecomposed felspar that is used as a pigment.

The separation is effected (Collins, *The Hensbarrow Granite District*, Truro, 1878) by washing down the soft rock with a current of water into large pits, where the coarse quartz settles, leaving the clayey water carrying the kaolin mixed with fine particles of sand and mica, which is thence run by means of troughs into a second series of pits to deposit these matters, and finally the creamy stream flows to large stone-lined tanks, where the kaolin settles as a thick mud. On running off the clear water, the kaolin is washed two or three times to improve the colour, and is then removed to the drying known as a Cornish "dry."

In Fig. 40 a plan is shown of the "dry" and settling tanks. A A represent the settling tanks which receive the

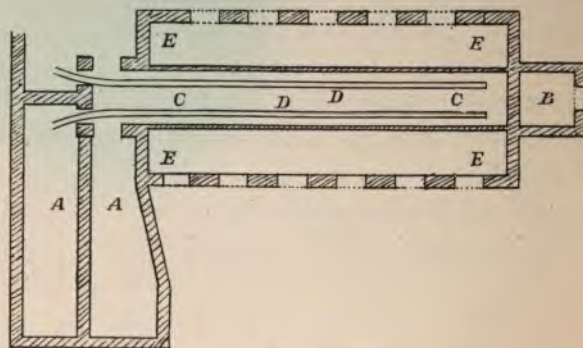


FIG. 40.

kaolin after being freed from quartz, mica, sand, etc.; on settling and washing, it is conveyed by the tramways D D to the floor of the drying shed C C, until it forms a layer 9 in. thick at the fire end and 6 in. at the stack end. The floor of the drying shed is made of large fire-clay tiles which cover a number of flues, 14 in. in width, and connected with the fire-place B. The tiles are 5 to 6 in. in thickness over the flues where the heat is greatest, and their thickness is reduced to $2\frac{1}{2}$ in. at the other end of

the building. The clay at the fire end is dried within twenty-four hours, while that deposited at the stack end, where the heat is well spent, requires two to three days. When dried, the clay is stored in the sheds E E E E.

Chalk or Whiting.—It is prepared from a soft earthy variety of limestone, and is chemically a carbonate of lime mixed with a small proportion of alumina, magnesia, and silica.

By crushing and elutriation, it is obtained as a soft white powder.

The Vienna white used by artists is a form of purified chalk.

Marble.—White marble used for statuary purposes, and ground to a very fine powder, is used in the manufacture of cheap paints.

It is quarried on the south-west slope of the Apuan Alps, Italy, and is mainly composed of carbonate of lime.

CHAPTER XIV.

DRYING OILS AND SICCATIVES.

Drying Oils.

FAT or fixed oils form the more important of the two great classes in which all natural oils are divided. In the pure state they are colourless or tinted a very pale yellow; commercially, they are found with shades varying from yellow to dark brown. The smell and taste vary with their degree of purity, and generally indicate the nature of their origin.

All the fat or fixed oils are insoluble in water, but are readily dissolved by petroleum, turpentine, and many of the volatile oils, ether, carbon disulphide, benzine, etc. On exposure to air, they have an attraction for and undergo a change; through the absorption of oxygen, some become rancid and sour, while others thicken and dry up to yellowish transparent resins. The former are termed non-drying oils, while the latter are known as drying oils, and are used as vehicles for pigments in painting.

All drying oils are of vegetable origin, and yield a more or less proportion of linoleic acid when saponified; the greater the quantity of this acid formed, the more rapidly the oil dries.

Various methods of extracting the oil from the seeds are in use, such as—(1) Dissolving out by petroleum spirit, benzine, or carbon disulphide; (2) crushing between the plates of a powerful press; or (3) by simply boiling the crushed seeds with water and skimming off the oil.

The oils yielded by these processes are crude and low in colour, and require for many purposes refining. This may be partially done by—(1) Mechanically washing with water, (2) filtration through animal charcoal, or (3) by prolonged exposure to the air, with frequent agitation.

The most efficient method, however, is by treatment with dilute sulphuric acid. For this purpose the oil is heated to 50° C. in a lead-lined vat provided with a steam coil, and, for every 300 gallons oil treated, 6 lb. of strong sulphuric acid, diluted with an equal weight of water, are well stirred in. The impurities are charred by the acid, and on settling to the bottom leave a clear supernatant oil, which requires to be further washed with water to remove all traces of the acid used.

The drying properties of the fat or fixed oils are greatly increased by boiling them alone, or with black oxide of manganese, litharge, sulphate of zinc, etc.; the product being then known as “boiled oil,” and from its highly siccative power can be used without the after addition of “dryers.”

The following are classed as drying oils:—

(a) *Linseed Oil*.—This oil is the most important of all the drying oils, and is extracted from the seeds of the *Linum usitatissimum*.

The following analyses by way represent the composition of linseed:—

	Nitrogen.	Fat.	Ash.	Water.
	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Riga	3·60	34·70	5·25	9·45
Memel	3·33	36·00	3·56	8·74
The Black Sea	3·31	38·42	5·64	10·22

In the expression, 24 to 26 per cent. of oil is extracted from the seeds, which contain 34 to 38 per cent. of oil; the

residual cake is largely used for cattle feeding, and retains from 10 to 12 per cent. of oil.

On the choice of seed depends the quality of the oil produced: a green unripe seed yields a thick turbid oil, bitter to the taste, and smells rancid; while the product from ripe seed appears limpid and pale, has little smell, and is sweet to the taste.

Pure linseed oil is nearly colourless, and has a density of .930 at 15° C., which is lowered to .881 at 100° C. The solidifying point is from -20° to -27° C. Chemically, it is composed of the glycerides of linolenic and isolinolenic acids with stearine.

When the oil is extracted in the cold, it is known as "cold drawn oil," and is lighter in colour and purer in body than when expressed by the aid of steam heat to the plates of the press, owing to the lesser quantity of stearine extracted with the oil.

For the manufacture of paints, the oil is either used in the "raw" state, or is boiled, and thence known as "boiled oil."

According to Fox, the chemical changes resulting from the boiling of linseed oil are the formation of highly oxidised bodies by the decomposition of the glycerides of the oil, while the glycerine splits up into acids of the acrylic series, whose vapours give that irritating smell which always accompanies oil boiling.

The boiling of linseed oil is carried out in copper cylindrical pans, either steam-jacketed or set over a furnace; the former, for safety, being the more preferable.

The raw oil having been run in to within 6 to 7 in. of the top, the heat, whether steam or open fire, is gradually applied until a temperature of 120° C. is reached; allow the gradual increase of heat to be spread over two hours, then bring the whole to a gentle "simmer," and keep at this for

four hours. During the "simmering" remove any scum appearing on the surface with a copper ladle, and add the black oxide of manganese, litharge, or sulphate of zinc, to be used, with frequent stirring. Continue the gentle boiling until a skin forms on the surface of the oil, then withdraw the heat, cover up and allow to settle for twenty-four hours, when the whole of the mucilage formed will have settled to the bottom. Ladle out the oil into a storage lead-lined vat, cover up, and allow it to stand until the oil becomes clear and transparent.

A better method of using the above "drying" agents is to weigh out the required quantity and tie it up in a bag, which is suspended in the copper pan. By this means the bag and its contents can be used for a second boiling, after being well washed with water.

The following are the proportions of "drying" agents used :—

- (1) *Dark Boiled Oil*.—1 gallon linseed oil ; $\frac{1}{2}$ lb. powdered litharge.
- (2) *Pale Boiled Oil*.—1 gallon linseed oil ; $\frac{1}{2}$ lb. sulphate of zinc.
- (3) *Very pale Boiled Oil*.—1 gallon pale linseed oil ; 1 lb. sulphate of zinc.

(b) *Rape-seed Oil*.—The seeds of the winter-rape (*Brassica napus*) yield, by pressing, about 35 per cent. of a yellowish oil, known as rape oil. It has a specific gravity of .912 at 15° C., and solidifies at - 4° C. The oil has a peculiar odour, and by dry distillation at about 300° C. it is decomposed, yielding the irritating vapours of acrolein along with gaseous hydrocarbons. It dries rapidly when exposed in thin layers.

(c) *Hemp-seed Oil*.—This oil has a greenish-yellow colour, which on keeping becomes brown. It is expressed by hydraulic pressure, from the seeds of the common hemp

(*Cannabis sativa*), which yield about 30 per cent. of oil, the residual cake being used to some extent for cattle feeding. The oil has a density of $\cdot 925$ at 15° C., and solidifies at -15° to -28° C. On treatment with sulphuric acid, the natural colour of the oil changes to intense green, and, with nitric acid, a greenish dirty brown. In presence of caustic soda solution, it forms a thick brownish-yellow liquid. It dries quickly.

(d) *Poppy-seed Oil*.—By expression, this oil is obtained from the seeds of the black poppy (*Papaver somniferum*). It is straw-yellow in colour, limpid, and odourless, and soluble in 25 parts cold or 6 parts boiling alcohol, and has a density of $\cdot 925$ at 15° C. On the addition of sulphuric or nitric acid, it turns a dirty white. When used as a drying oil, it is previously bleached by exposure to the sun in shallow vessels containing a layer of salt water.

(e) *Walnut Oil*.—Walnut oil is of a greenish-yellow colour, and is extracted from the ripe kernels of the *Juglans regia*. It has an agreeable faint smell, with a nutty taste. At 15° C. the density is $\cdot 925$, and it solidifies at -18° to -28° C. The oil is but moderately soluble in alcohol, and is highly siccative.

(f) *Niger-seed Oil*.—This oil is pressed from the seeds of the *Guizotia regia*. It is pale yellow in colour, sweet to the taste, and dries very rapidly on exposure in thin layers. The density is $\cdot 926$ at 15° C., and it solidifies at -9° C.

Oils extracted from the deadly nightshade (*Atropa belladonna*), grape seed (*Vitis vinifera*), gold of pleasure seed (*Camelina sativa*), weld seed (*Reseda luteola*), tobacco seed (*Nicotiana tabacum*), and Scotch fir seed (*Pinus sylvestris*), all possess high drying powers on exposure; they are, however, but rarely used in the grinding of pigments for painting.

Siccatives.

Under the name of siccatives, certain chemical agents are added to ground pigments before using, in order to increase their drying and hardening properties.

As they, to some extent, detract from the delicacy of the colours with which they are mixed, they should be avoided in the finishing coats of delicate colours. Again, they should not be employed with ground pigments that dry well, nor, when used, should an excess be mixed with the paint, as this retards the drying. Siccatives should only be added to the colour when about to be used.

The following are the principal siccatives in use:—

(a) *Sulphate of Manganese.*—This salt is prepared by burning black oxide of manganese mixed with about one-tenth of its weight of powdered coal in a gas retort. The manganous oxide formed, is raked out, and then treated in a lead-lined vat provided with a steam coil, with sulphuric acid. When completely dissolved, the liquor is run into shallow crystallizing vats. After crystallization, the crystals are removed and drained.

It may also be prepared by dissolving manganous carbonate in dilute sulphuric acid, and crystallizing as before.

The crystals of sulphate of manganese generally are tinted with a faint amethyst colour, due to the presence of slight quantities of a manganic salt. They are soluble in their own weight of water, moderately soluble only in weak alcohol, and completely insoluble in absolute alcohol.

(b) *Acetate of Manganese.*—The acetate is prepared as a “dryer” by dissolving manganous oxide, prepared from the black oxide, in acetic acid, and then evaporating the resulting solution until the crystals begin to form on the surface; the liquor is then run into crystallizers, from whence the crop of crystals formed, is removed and drained. The crystals have

a pale rose-coloured tint, and are soluble in 3 parts cold water.

(c) *Borate of Manganese*.—When borax is added to a solution of sulphate of manganese, a dense crystalline precipitate of borate of manganese is formed, which is washed on a filter, and then dried.

(d) *Oxalate of Manganese*.—This salt is produced when a solution of sulphate of manganese is treated with oxalic acid. The precipitated salt, after washing and drying, has a faint violet tint, and is moderately soluble in hot water.

(e) *Benzoate of Manganese*.—To prepare this salt, benzoic acid is dissolved in boiling water, and the solution carefully neutralised with manganous carbonate. When the effervescence has subsided, filter off any excess of the carbonate added, and evaporate the filtrate to dryness. The benzoate of manganese thus prepared, is an amorphous, hard, brownish material, which may be powdered and kept in the pulverised state in any climate.

(f) *Resinate of Manganese*.—Dissolve a resinate of potash or soda in hot water, and to the solution add chloride of manganese. The precipitated resinate of manganese formed, is collected on a filter, washed, and then dried.

(g) *Borate of Zinc*.—On adding borax to a hot solution of sulphate of zinc, and then boiling for some time, a white borate of zinc is precipitated, which is collected on a filter, washed with hot water, and then dried.

(h) *Resinate of Cobalt*.—This compound is prepared in the same way as resinate of manganese, but substituting chloride of cobalt in place of chloride of manganese.

(i) *Resinate of Magnesia*.—When a solution of resinate of potash or soda is treated with chloride or sulphate of magnesia, a gelatinous precipitate of resinate of magnesia is formed, which is run on to a filter, washed with water, and then

dried. It is soluble in coal-tar naphtha, strong alcohol, and hot linseed oil.

(j) *Hippuric or Urobenzoic Acid*.—This product has been used with success as a “dryer.” It can be made artificially by heating glycocine in a sealed tube with benzoic acid, also by heating the zinc salt of glycocine with chloride of benzoyl to 120° C. On the large scale, it is prepared from the urine of horses and cows by treating it with milk of lime, and supersaturating the hippurate of lime formed, with hydrochloric acid. The crude brownish acid thus produced, is purified by further treatment with boiling water and milk of lime, and then finally saturated with hydrochloric acid. Hippuric acid forms colourless transparent prisms, which melt at a gentle heat, solidifying to a crystalline mass on cooling. It is sparingly soluble in cold water, but readily dissolves in boiling water and alcohol.

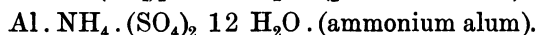
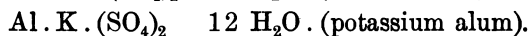
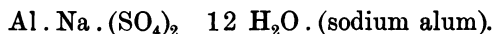
(k) *Acetate of Lead* (known as Sugar of Lead).—See “Salts of Lead,” p. 32.

(l) *Litharge*.—See “Oxide of Lead,” p. 109.

(m) *Oxide of Zinc*.—See “Oxide of Zinc,” p. 166.

(n) *Sulphate of Zinc*.—See “Salts of Zinc,” p. 163.

(o) *Burnt Alum*.—The double salts of aluminic sulphate, with sodium, potassium, or ammonium sulphates, form what are technically known as alums. They crystallize in regular octahedrons, and contain 12 atoms of water, thus—



On heating to 200° C., the whole of the water of crystallization is expelled, leaving a powdery substance known as “burnt alum,” and in this form it is used as a dryer.

(p) *Borax*.—Biborate of soda or borax is obtained in the anhydrous state by fusing 124 parts of boric acid with 53

CHAPTER XV.

OIL OF TURPENTINE.

OIL of turpentine belongs to that class of oils known as essential or volatile oils, and may be easily distinguished from a fatty or fixed oil, not only by the smell, but also by allowing a drop of each to fall on a piece of white paper; with turpentine, the translucent spot-former disappears on exposure to air or slight heating, whereas the stain of the fat oil remains permanent. Turpentine is composed of carbon and hydrogen, has a peculiar odour, boils at 160°C ., and on distillation it passes over unchanged, leaving practically no residue at 180°C .

It does not mix with water, but is miscible with ether and alcohol, and dissolves readily the resins, camphors, and many hydrocarbons. The turpentines of commerce are mainly the American, extracted from the *Pinus Australis*, and the French, from the *Pinus maritima*. Both are similar in their constitution and properties. From the incisions made in the trees, a thick resinous oil exudes, which is collected and then distilled in large copper stills, each having a capacity of 600 gallons, and provided with a dome or head to which is affixed the condenser pipe. They are heated by an enclosed fire, or, preferably, as adopted by French distillers, by steam coils. To the stills are first added water, and then the crude oil, freed from bark, leaves, and other foreign matter, is run in from the storage tanks, and the temperature is gradually raised to 160°C ., and kept

about that point until the finish. Meanwhile the oil and water coming over are condensed and run into receivers, the distiller testing the layer of oil from time to time.

When the proportions, by volume, of the oil and water distilling over, are about the ratio of 1 to 9, the process is stopped, in order that the colour of the oil shall not be lowered by any volatile organic matter. After separation of the water, the oil is pumped to storage tanks to settle.

The yield averages 12 per cent. by weight of the crude oil.

On completion of the distillation, the heat is withdrawn, and the air valves are opened, and the residual liquid matter in the still is run from a pipe and cock fixed near the bottom, passed through a strainer to remove any scum or dirt, and thence into barrels to solidify, forming the colophony or common resin of commerce. This product has an extensive use, and is of a dark brown colour when made from American crude oil; the pale amber variety is the residue of the French crude oil, and is known as "virgin rosin."

Resin is insoluble in water, but dissolves in solutions of the alkalies forming resin soaps, also in benzine, chloroform, and ether.

Resin or Rosin Oil.

This oil, used largely in the manufacture of greases, soaps, etc., is the product from the dry distillation of resin.

The operation is carried on in cast-iron stills of about 5 tons capacity, encased with brickwork and heated by fires beneath. Each still is provided with a copper worm, connected at the upper end with the condenser pipe, and, at the lower, with the receiver, into which the products of distillation flow.

During the early stage of the operation, uncondensable hydrocarbons and carbonic acid gas are given off in considerable quantities; between 90° and 280° C., the distillate is collected apart, and is known as "rosin spirit," being used principally as a substitute for turpentine and in varnish-making. It is refined by agitating with caustic soda, washing, and then re-distilling the washed spirit. On changing the receivers the temperature in the still is gradually raised to 400° C., and between 300° and 400° C. a mixture of heavy hydrocarbons with phenols and undecomposed resin, come over, yielding on condensation the crude oil known as resin or rosin oil. The residue in the still is pitch. A ton of resin yields about 7 gallons of spirit and 17 cwt. of heavy resin oil.

Crude resin oil is strongly fluorescent; the "bloom," however, can be removed by treatment with dinitronaphthalene, or by washing with soda lye, then with water, and afterwards exposing the treated oil in shallow trays to the air.

Pigments.

Although some pigments are from animal and vegetable sources, it may be said generally, that they are of a mineral origin and are brought into commerce either in the native or manufactured state as sulphides, oxides, or metallic salts.

When ground to a fine state of division with a suitable oil, they are known as paints, and in this form are capable of being spread over surfaces with a brush. The economical value of a pigment depends on its opacity and density; those existing in an opaque and amorphous form absorb more oil, and thus have greater "body" or "covering power" than those of a crystalline texture. From this difference in their physical form, Dutch white lead owes its superiority over many pigments of a crystalline nature.

The permanence of a pigment is affected by several chemical changes. For instance, the pigments of lead, copper, bismuth, and partly those of mercury, darken by exposure to a polluted atmosphere, through the action of sulphuretted hydrogen present forming sulphides. On the other hand, the pigments of zinc and barium remain unaffected by the gas, and thus retain their whiteness. Some pigments are affected by the oxygen of the atmosphere, when exposed: some of the chromates, for instance, gradually turn green; others, again, are acted upon by the "dryers" used, the chemical reaction altering the nature of the paint.

CHAPTER XVI.

CLASSIFICATION OF MINERAL PIGMENTS ACCORDING TO THEIR COLOUR.

Whites.

Dutch White Lead.—Basic Carbonate of Lead, p. 112.

Hannay's White Lead.—Sulphate of Lead, p. 133.

Pattison's White Lead.—Oxychloride of Lead, p. 39.

Sulphite White Lead.—Sulphite of Lead, p. 139.

Pearl White.—Basic Nitrate of Bismuth, p. 139.

Strontian White.—Sulphate of Strontium, p. 139.

Magnesia White.—Oxide and Carbonate of Magnesia, p.

140.

Tungsten White.—Tungstate of Barium, p. 140.

Cadmium White.—Hydrate of Cadmium, p. 140.

Antimony White.—Oxide of Antimony, p. 140.

<i>Fine White</i>	}	Basic Carbonate of Lead.
<i>Krems White</i>		
<i>Flake White</i>		

<i>Venice White</i>	}	Mixtures of White Lead and Sulphate of Barium, p. 141.
<i>Dutch White</i>		
<i>Hamburg White</i>		

<i>Baryta White</i>	}	Sulphate of Barium, p. 176.
<i>Permanent White</i>		
<i>Blanc Fixe</i>		

Spanish White.—Carbonate of Lime, p. 179.

<i>Zinc White</i>	}	Oxide of Zinc, p. 166.
<i>Chinese White</i>		

Lithophone White.—Sulphide of Zinc, p. 165.

Charlton White.—Mixture of Sulphide of Zinc with Sulphates of Barium and Strontium, p. 166.

Griffith's White.—Sulphide of Zinc, p. 165.

Derbyshire White.—Finely divided Chalk, p. 179.

Yellows.

Chrome Yellow }
Paris Yellow } Neutral Chromate of Lead.

This pigment is prepared by dissolving bichromate of potash in water, and adding to slight excess a solution of acetate of lead. The yellow precipitate formed, is washed by decantation, and then dried.

Cologne Yellow.—Neutral Chromate of Lead, toned down by the addition of Sulphate of Barium (Barytes).

The shade also may be produced by digesting 3 parts sulphate of lead with 1 part chromate of potash dissolved in water. The mixed precipitate of sulphate and chromate of lead is washed and dried.

Zinc Yellow.—Neutral Chromate of Zinc, p. 163.

Strontian Yellow.—Neutral Chromate of Strontium.

It is made by adding to a solution of bichromate of potash excess of a solution of nitrate or chloride of strontium, and filtering, washing, and drying.

Baryta Yellow }
Lemon Yellow } Chromate of Barium.

Prepared by mixing solutions of bichromate of potash and nitrate or chloride of barium together, the latter in slight excess, then washing and drying the precipitated chromate of barium.

Bismuth Yellow.—Chromate of Bismuth.

On adding bichromate of potash to an acid solution of nitrate of bismuth, a yellow flocculent precipitate of chromate

of bismuth is produced, which, on filtering, washing, and drying, yields the pigment.

Cadmium Yellow.—Sulphide of Cadmium.

This lemon-yellow pigment is prepared by adding potassium or sodium sulphide to a solution of nitrate of cadmium. The precipitated sulphide is washed and dried. It is to some extent affected by light.

Aureolin.—Double Nitrite of Cobalt and Potassium.

Cobalt yellow, as it is sometimes termed, is a pigment produced by adding nitrite of potash to a solution of chloride or nitrate of cobalt, and then filtering, washing, and drying the yellow precipitate.

<i>Stone Yellow</i>	} Argillaceous Earths containing hydrate of iron.
<i>Oxford Ochre</i>	
<i>Yellow Ochre</i>	

In the native state they are found of fine quality, and require simply washing before being brought into the market. On calcination they turn red. Artificially, a yellow ochre may be prepared from ferrous sulphate, by precipitation with an alkali, and exposing the precipitate formed, to the action of air.

Naples Yellow.—Oxides of Antimony and Lead.

This pigment is formed by first calcining a mixture of 3 parts metallic antimony, 1 part oxide of zinc, and 2 parts red lead, then grinding the calcined mass to a powder and fusing in a closed crucible at a red heat for five hours. The fused mass on cooling is ground to a fine powder, washed and dried.

King's Yellow.—Sulphide of Arsenic.

It is found in the native state, and is also prepared artificially, by subliming a mixture of arsenious acid with sulphur, or by precipitating a solution of arsenious acid with sulphuretted hydrogen gas.

Cassel Yellow.—Oxychloride of Lead, p. 40.

Chrome Orange.—Basic chromate of lead is the base of all chrome orange colours. They are produced when the acetate of lead used in the production of chrome yellow is of a basic nature, instead of being neutral. Burnt sienna, prepared by calcining raw sienna, and burnt Roman ochre calcined from Roman ochre, are pigments of an orange shade.

Greens.

Chrome Green.—Hydrated Oxide of Chromium.

This pigment is prepared by fusing, in a crucible, equivalent quantities of anhydrous boracic acid and bichromate of potash, and then treating the fused mass with hot water. The hydrated oxide is washed and finely trituated. The common quality of chrome green is a mixture of chrome yellow and Prussian blue.

Brighton Green.—Acetate of Copper and Whiting.

It is prepared by stirring whiting to a pasty consistency in a mixture of sulphate of copper and acetate of lead dissolved in water. The paste, after draining, is dried and ground to a powder.

Manganese Green.—Oxides of Manganese and Barium.

Mix intimately 2 parts hydrate of barium, 1 part nitrate of barium, and 1 part oxide of manganese, and fuse the mixture in a crucible heated to dull redness. Pour the fused mass on to a slab, and, when solid, crush to a powder, and boil well with water, filter and dry.

<i>Cobalt Green</i>	} Phosphates of Zinc and Cobalt, p.
<i>Rinmann's Green</i>	
	162.

Vienna Green.—Arsenite of Copper.

This arsenical pigment is prepared by making a solution of 10 parts sulphate of copper and 1 part unslacked lime with acetic acid, and stirring in a boiling solution of 10 parts arsenious acid. The green precipitate is collected on a cloth filter, washed well, dried, and ground to fine powder.

Scheele's Green.—Arsenite of Copper.

Formed by dissolving arsenious acid in a solution of potash, and then gradually adding a boiling solution of sulphate of copper. Filter, wash well, and dry.

Mineral Green.—Carbonate of copper.

It is found native as malachite; artificially, it is precipitated when a solution of carbonate of soda is added to a solution of copper sulphate.

Brunswick Green.—Hydrate of Copper.

This deep and rich green is formed when carbonate of ammonia is added to a mixed solution of equal parts of alum and copper sulphate. The precipitate is collected on a cloth filter, washed and dried. Various shades of green can be produced by altering the proportions of alum used.

Blues.

Ultramarine.—Natural ultramarine is a deep blue pigment extracted from pure lapis-lazuli; owing, however, to its costly extraction, but little of the natural product is used in the arts. Artificially, it exists as a compound of silicates of soda and alumina with sulphide of sodium, and is manufactured in considerable quantities by grinding together 10 parts pure kaolin, 9 parts soda ash, 11 parts sulphur, and 2 parts charcoal. The ground mixture is heated to bright redness for twelve to sixteen hours in crucibles, or in a "mass" oven, until a sample withdrawn shows a greenish-blue shade, which, on cooling, becomes a deep blue. When the sample indicates that the mass is sufficiently burnt, the oven is hermetically closed, and allowed to cool for a week. On opening, the calcined mass is withdrawn, freed from any brown parts due to overheating, crushed, and then washed in vats having perforated false bottoms from any soluble impurities. The washed ultramarine is dried on kilns, then sifted through a fine sieve, and finally sorted according to shade.

Cobalt Blue }
Thenard's Blue } Phosphate and Aluminate of Cobalt.

The blue pigment known by the above names is prepared by heating to dull redness a mixture of 10 parts freshly precipitated and dried alumina and 1 part phosphate of cobalt. By artificial light, the shade appears violet.

Cyanine Blue }
Leitch's Blue } Cobalt Blue mixed with Prussian Blue.

Azure Blue }
Paris Blue } Artificial Ultramarine.

Prussian Blue.—Hydrated Ferric Ferrocyanide.

Pure Prussian blue can only be obtained by treating a solution of ferrocyanide of potassium with ferric chloride or other ferric salt. The commercial pigment is prepared on the large scale by dissolving 100 parts of ferrocyanide of potassium (yellow prussiate) in water, and then adding a solution of 80 parts ferrous sulphate, at the ordinary temperature. The mixture is now diluted with an equal bulk of water, brought to the boil, and, on the addition of 30 parts nitric acid (28° B.) and 15 parts strong sulphuric acid, the deep blue precipitate of Prussian blue is formed. The pigment is filtered through a cloth filter, and then dried. Prussian blue has a coppery lustre, is inodorous, tasteless, and non-poisonous, and possesses great body and covering power.

Saxon Blue.—This pigment consists of a mixture of alumina with potassio-ferric ferrocyanide. It is an inferior blue, and is prepared by precipitating a solution of ferrocyanide of potassium with 1 part ferrous sulphate and 3 parts alum, dissolved in water.

Reds.

Nearly all the red pigments of a mineral character found in commerce, are derived by the calcination of (1) natural

earths or ochres, formed of hydrate of iron combined with various proportions of clay, and (2) of sulphate or oxide of iron. Mars red, Indian red, light red, Venetian red, red ochre, are pigments derived from either of the two sources.

Vermillion Red.—Sulphide of Mercury.

This pigment is the richest of all the red colours. It is permanent, and possesses great body and covering power. The first stage of the manufacture consists of the formation of a crude sulphide of mercury by heating in an iron pan a mixture of 270 parts of mercury and $37\frac{1}{2}$ parts ground sulphur. On cooling, the mass is powdered, and then charged by portions into subliming pots made of refractory clay, and heated from below. After each charge, the vermilion sublimes in the upper parts of the pot, and at the finish the pots are withdrawn, cooled, and the bright red vermilion extracted. It is ground in a mill, washed, and then dried.

Vermillion is often adulterated with inferior red pigments, as chrome red, red ochre, and red lead.

Vermillion Scarlet.—Iodide of Mercury.

This brilliant shade is produced by adding iodide of potash to a soluble salt of mercury; the precipitate is then washed and dried.

Red Lead.—Tetroxide of Lead, p. 117.

<i>Chrome Red</i>	}	Basic Chromate of Lead.
<i>Persian Red</i>		

This pigment can be produced by boiling neutral chromate of lead or chrome yellow with half its weight of lime or caustic soda.

Browns.

Brown pigments of a mineral origin, are practically all derived from native ochres. Vandyck brown, Verona brown, Caledonian brown, and others, are all native ochres, raw or calcined.

Blacks.

Bone black, ivory black, lamp black, asphaltum black, and vegetable black have either an animal or vegetable origin.

The following table shows the stability in oils of different mineral pigments (Church, *Chemistry of Paints and Painting*):

Permanent.	Somewhat Changeable.	Untrustworthy.
Baryta white.	Aureolin.	King's yellow.
Zinc white.	Baryta yellow.	Zinc chromate.
Flake white.	Indian yellow.	Bituminous Vandyck brown.
Yellow ochre.	Strontian yellow.	
Raw sienna.	Chrome yellow.	
Vermillion.	Cobalt green.	
Indian red.	Emerald green.	
Venetian red.	Malachite.	
Light red.	Prussian blue.	
Red ochre.	Cologne earth.	
Ultramarine.	Earthy Vandyck brown.	
Burnt sienna.		
Raw umber.		
Burnt umber.		
Cappagh brown.		
Caledonian brown.		
Prussian brown.		

All the pigments of copper, lead, and bismuth darken on exposure to sulphuretted hydrogen gas, while zinc and barium whites are unaffected.

PAINTS.

Paints are pigments ground up with a suitable medium, such as linseed oil, either in a "raw" or "boiled" condition, and can be stained with a mineral colouring matter to any tint desired. They are produced as a thick paste, and should contain about 75 per cent. of the pigment with 25 per cent. of oil. To prepare the paste for use with the brush, it is thinned down with turpentine alone, or with turpentine and linseed oil, and the requisite quantity of siccative added, to enable the paint to dry quickly.

A paint ready for use, to fulfil all the requirements of a covering or protecting agent to surfaces on which it is applied, should spread well, or, in other words, have good covering power, under the brush, and yet be sufficiently viscous so that it will adhere without running. When applied, it should also leave coats of equal thickness, each coat should dry hard, without any tendency to peel or rub off, and be unaffected by any climatic influences.

The following are the mixings of some white market paints:—

- (1) 100 lb. zinc white ground in 22 lb. refined linseed oil.
- (2) 100 lb. zinc white, 40 lb. sublimed lead (sulphate of lead), 60 lb. English Paris white, ground with $12\frac{1}{2}$ gallons raw linseed oil and 1 gallon benzine dryer.
- (3) 400 lb. sublimed lead (sulphate of lead), 100 lb. Dutch white lead, ground to a paste with 12 gallons linseed oil, and thinned with 7 gallons oil dryer, 14 gallons raw linseed oil, and 7 gallons emulsion, prepared from linseed oil and lime-water.
- (4) 1400 lb. sublimed lead, 340 lb. zinc white, 450 lb. Paris white, ground with 100 gallons linseed oil, 25 gallons benzine, 40 gallons silica solution (equal parts of sugar of lead solution 3° B., and water glass solution 8° B.), 4 gallons oil dryer (prepared by taking 5 gallons raw linseed oil, place in varnish kettle, heat to 300° F., and 10 lb. powdered flake litharge, and 1 lb. varnish lime. Heat till it has a consistency equal to thick molasses and will string strongly. Cool to 250° F. and add 150 gallons naphtha), and 25 gallons turpentine.
- (5) 600 lb. sublimed lead (sulphate of lead), 600 lb. oxide of zinc, 300 lb. Dutch white lead, ground in

250 lb. raw linseed oil, and thinned with 44 gallons boiled linseed oil, 32 gallons raw linseed oil, 11 gallons oil dryer, $16\frac{1}{2}$ gallons silica solution. (*Board of Trade Journal.*)

In preparing a coloured paint for general work, the colour-mixer first produces a sample of the tint required, and then makes up the body of the paint with a white pigment and oil ground together. The colouring pigment is now added, the quantity being regulated by the shade of the sample. When the whole is mixed and matched, the proportion of dryers is added, and then the coloured paste is thinned down to a creamy consistence with turpentine. In the production of coloured paints the body should be of white lead only : for cheapness, however, inferior white pigments of little or no body or covering power are now added to the lead pigment.

Special classes of paints, in which the ingredients to some extent are similar to those found in ordinary white or coloured paints, are brought into the market to fulfil certain requirements. These may be classed as (1) fire-proof paints, (2) preservative paints, (3) enamel paints, and (4) so-called luminous paints.

Fire-proof paints consist largely of asbestos mixed with silicates incorporated with linseed oil.

The anti-fouling and anti-corrosive compositions are mainly prepared from zinc oxide and sulphide ground with a varnish made of naphtha, rosin, and gum. They are chiefly used for ships' bottoms.

For iron surfaces, red lead forms an effective coating when mixed with oil.

Enamel paints are used for decorative purposes, and are made by grinding a mineral pigment with a varnish, and tinting to requirements.

CHAPTER XVII.

ANALYSIS OF RAW AND FINISHED PRODUCTS.

Lead Ores.—The estimation of lead is made by a dry assay or by precipitation.

Galena.—(a) *By Dry Assay.*—The assaying of galena ore is best carried out by the iron process, which depends on the fact that at a red heat this metal decomposes sulphide of lead with the formation of sulphide of iron and metallic lead. It is made in an iron crucible, which thus supplies the decomposing agent. An average sample of the ore is first crushed to a fine powder, sieved, and 20 grms. weighed out. The flux used is a mixture of 2 parts fused borax and 1 part dry carbonate of sodium in a fine state of division, 20 grms. being taken and intimately mixed with the weighed ore. In charging, the crucible is first brought to a dull red heat in a coke furnace, and then the mixture of ore and flux carefully added. On raising the temperature to redness, the contents of the crucible liquefy with evolution of carbonic acid gas. When the mass has become quiescent, the crucible is partly removed from the fire and the contents stirred with an iron rod. On replacing in the furnace, the heat is raised to bright redness for five minutes to effect the complete decomposition of the sulphide of lead. Now remove the crucible and pour the contents into an iron mould, taking care that any metallic beads of lead which may attach themselves to the sides of the crucible are removed and added to the mould. When cold, the button of metallic lead with its covering of slag is easily removed,

broken, and the button separated. On washing and brushing to remove any adhering particles of slag, the button is dried and weighed, and an opinion formed of its quality by its colour and softness.

If the ore contains antimony it will be found, on reduction, in the button of lead, and giving to it a certain hardness. In the assay, the antimony can be oxidised and thus retained in the slag by using a little nitrate of potash with the flux. The whole of the silver in the ore is reduced and found incorporated with the lead, and to estimate the amount the button undergoes the process of cupellation, by which the lead is oxidised to litharge, leaving the silver untouched (see Percy's *Metallurgy of Lead and Silver*). Cerusite, or carbonate of lead, anglesite, or sulphate of lead, and other lead ores, are assayed in a similar manner, using, however, an earthen crucible instead of an iron one, and fusing with a flux composed of 6 grms. argol, 18 grms. carbonate of sodium, and 12 grms. of salt, to every 15 grms. of ore taken.

In estimating the lead in fumes, cupel bottoms, and refractory slags, the flux used is a mixture of 13 grms. argol, 26 grms. carbonate of sodium, and 13 grms. fused borax, the whole being ground to a fine powder and intimately mixed with 26 grms. of the slags, etc., reduced to a fine condition. The treatment in the furnace and the after-separation of the button of lead is similar to that of galena; the reduction, however, is carried out in an earthen crucible.

(b) *By Precipitation.*—Take an average sample of the galena ore, crush finely, and pass the whole through a sieve of fine mesh. Take a porcelain crucible and weigh out 3 grms. of the powdered ore, add 20 c.c. of strong nitric acid, and heat on a sand-bath for fifteen minutes, then mix with 15 c.c. strong sulphuric acid, and continue the evaporation nearly to dryness. Cool, add a few drops of sulphuric acid and about 50 c.c. of water, heat nearly to boiling, and filter, washing the

residue with hot water until the filtrate is free of any acidity. Now wash the residue, which is mainly sulphate of lead, into a beaker with the least possible quantity of hot water, and add 100 c.c. of a dilute solution of carbonate of sodium, and bring the whole to the boil for ten minutes. Throw on to a filter and wash the precipitate with hot water until the washings are no longer alkaline. The precipitate is carbonate of lead, along with any insoluble foreign matter, as silica, etc. Wash into a beaker with as small a quantity of water as possible, and slowly add strong acetic acid till the solution is acid; the effervescence is due to the liberation of carbonic acid gas, and care must be taken that no loss is occasioned by spurting. Boil for a few minutes, and then allow to stand for a time. Filter and wash well with hot water. The residue on the filter is the insoluble matter, silica, etc., while the filtrate contains the whole of the lead as soluble acetate. If the filtrate is bulky, it is concentrated by slowly evaporating on the water-bath, and then dilute sulphuric acid until no further precipitate is formed; heat for ten minutes, and filter. The precipitate of sulphate of lead is washed with hot water, dried, ignited, and weighed as PbSO_4 , and from the amount found the lead is calculated.

Example—

Weight of ore taken	3	grms.
Weight of PbSO_4 found	3.7	„
Equivalent to metallic lead	2.53	„
Then $\frac{2.53 \times 100}{3} = 84.33$ per cent. of lead in the ore.		

Zinc Ores.—The estimation of zinc in calamine and blende, the ores of zinc used for metallurgical purposes, is conducted in the wet way by precipitation.

(a) *Calamine.*—Five grms. of the ore finely powdered are weighed out into a beaker, and treated cautiously with 10 c.c. strong sulphuric acid; after the effervescence has subsided,

place the beaker on sand-bath and evaporate to dryness, then cool, add a few drops of hydrochloric acid and a little water and bring to the boil. Filter and wash well with hot water. Neglect the residue, and to the filtrate add sulphuretted hydrogen until no further precipitate is formed. Throw on to a filter and wash well with sulphuretted hydrogen water. The precipitate formed is sulphide of zinc, which is completely dissolved in nitric acid, then make the solution strongly alkaline with carbonate of sodium, and filter off the precipitated carbonate of zinc, wash with hot water, dry, ignite, and weigh as oxide of zinc, from which the amount of zinc is calculated.

Example—

Weight of ore taken	5	grms.
Weight of ZnO found	2.81	„
Equivalent to metallic zinc	2.26	„
Then $\frac{2.26 \times 100}{5} = 45.20$ per cent. of zinc in the ore.		

(b) *Blende*.—The analysis is carried out in a manner similar to that of calamine, excepting that the ore is dissolved in a mixture of nitric and hydrochloric acids. The metal is precipitated as zinc carbonate, with sodium carbonate, which, after washing, is dried, ignited, and weighed as oxide of zinc, and from the result the percentage of zinc is calculated.

Example—

Weight of ore taken	5	grms.
Weight of ZnO found	3.32	„
Equivalent to metallic zinc	2.66	„
Then $\frac{2.66 \times 100}{5} = 53.20$ per cent. of zinc in the ore.		

Iron in Commercial Zinc.

To detect in a simple way the presence of iron in zinc, Fresenius dissolves the metal in dilute sulphuric acid, in a small flask provided with a gas evolution tube, the outer limb

of which is placed under water. After the solution of the metal is completed, the water is allowed to partly recede into the flask, then completely cool, and add, drop by drop, a dilute solution of potassium permanganate. If a drop indicates the same red tint to the solution of zinc as to an equal volume of acidulated water, the zinc may be considered free from iron.

Analysis of White Lead Paint.

A genuine lead paint should consist only of Dutch corroded white lead ground up with its proper proportion of linseed oil. In commerce many so-called white lead paints are found made up with a minimum of genuine lead and a maximum of cheap materials, such as clay, carbonate of lime, carbonate of barium, sulphate of barium, oxide and sulphide of zinc, etc., and ground, not with good linseed oil alone, but with a mixture of linseed with mineral oils. Rosin oil and rosin spirit are also used as adulterants. The following form of analysis, devised by Stillman, and which gives very reliable results, will enable an estimate to be made of the value of a sample submitted. Into a 150 c.c. flask weigh 10 grms. of the paint to be examined, and add 50 c.c. of ether by means of a pipette, shake to mix the whole together, then cork and set aside for two hours. Then pour the contents on to a filter, collecting the filtrate in a tared beaker, wash the flask completely with ether, and add the washings to the filter. The residue on the filter contains the whole of the mineral matter of the paint, while in the filtrate are found the oils used. Label the filter No. 1, and place on one side, and proceed with the filtrate as follows:—Place the beaker containing the filtrate in the air oven and heat to 105°C ., which evaporates the ether and any moisture present, and re-weigh. The result is the total weight of oil or oils present in the sample. If mineral oil has been found during a qualitative testing, add to the tared beaker about 50 c.c. of an alcoholic solution of potash,

and evaporate in the air oven until the whole of the alcohol is expelled; the result is the formation of a soap by the saponification of the linseed oil present, the mineral oil remaining unacted on. Now add 60 c.c. of water to dissolve the soap, and transfer the contents of the beaker to a separating funnel, with the addition of about 30 c.c. of ether. Shake well and set aside for ten hours to allow a complete separation. The water, in which is dissolved the soap formed, is now drawn off, leaving the mineral oil unsaponified in the ether solution. Draw off the latter into a tared porcelain dish and evaporate in the air oven at 105°C . for eight hours, and then re-weigh the dish. The difference in weight indicates the amount of mineral oil present, and this, subtracted from the total weight of oils found, gives the amount of linseed oil present in the sample.

Example—

10 grams. of sample taken.			
Total weight of oils found	2.500	grms.	
Weight of mineral oil found606	„	
Leaving linseed oil	1.894	„	
The percentage then is $1.894 \times 10 = 18.94$ linseed oil.			
$.606 \times 10 = 6.06$ mineral oil.			

The filter No. 1 is treated as follows:—

The residue on the filter contains all the mineral present in the paint. It is dried, and the paper and contents then placed in a beaker and treated with hot acetic acid; a little water is added, and the whole brought nearly to the boil, then filter and wash with boiling water.

The residue on the filter may contain any sulphates of baryta, lead or lime, clay, silica, etc.; place on one side, and label No. 2. The filtrate contains lead, zinc, barium, and lime, previously existing in the paint as carbonates. Add sulphuretted hydrogen water until no further precipitate is

produced, and filter, washing the precipitate with the same re-agent. Mark the filtrate No. 2, and place on one side. The residue contains lead and zinc as sulphides, which are completely dissolved in nitric acid; sulphuric acid is then added, and the liquor evaporated nearly to dryness on a water-bath; add a little water and wash the whole on to a filter, wash with hot water, dry, ignite, and weigh as sulphate of lead (PbSO_4), and from the data obtained calculate to the basic carbonate of lead ($2\text{PbCO}_3 \cdot \text{PbH}_2\text{O}_2$). The filtrate contains the zinc, the solution is made alkaline with carbonate of soda, and then boiled; the precipitate of carbonate of zinc is collected on a filter, washed until free from alkali with hot water, and it is then dried, ignited, and weighed as oxide (ZnO). If sulphide of zinc has been found in the qualitative test to have been used with the oxide, the calculation is then made on the oxide and sulphide of zinc ($\text{ZnO} \cdot \text{ZnS}$). The filtrate marked No. 2 is now boiled to get rid of the sulphuretted hydrogen, hydrochloric acid added to excess, and then dilute sulphuric acid; the precipitate of sulphate of barium is filtered, washed with hot water, dried, and weighed as sulphate of barium (BaSO_4). If the barium salt existed as carbonate in the original sample, it is calculated as BaCO_3 . In the filtrate, which is rendered alkaline with ammonia, the lime is precipitated as oxalate by the addition of oxalate of ammonia, and the precipitate, after washing and drying, is ignited in a muffle furnace and weighed as lime, from which the carbonate (CaCO_3) is calculated. The residue on the filter marked No. 2 is now transferred to a small flask, and digested in the cold for twelve hours with a saturated solution of carbonate of ammonia, or, still better, a few lumps of the carbonate are added. Filter and wash well, throw away the filtrate, and treat the residue with hot acetic acid in a small flask, then filter. The residue contains sulphate of barium, silica,

and clay; label No. 3, and place on one side; the filtrate contains the lead and lime acetates. Saturate the solution with sulphuretted hydrogen, whereby the lead is precipitated as sulphide. Filter off the precipitated sulphide, wash with sulphuretted hydrogen, dry, and then transfer the residue to a porcelain crucible; add nitric acid and evaporate with a few drops of sulphuric acid nearly to dryness; add a little water, and wash the contents of crucible on to a filter; wash with hot water, dry, ignite, and weigh as sulphate of lead (PbSO_4). The filtrate from the lead precipitate is boiled to expel the sulphuretted hydrogen, and then rendered alkaline with ammonia; oxalate of ammonia is now added, and the precipitated oxalate of lime is washed, dried, ignited in a muffle furnace, and weighed as lime (CaO), and then calculated to sulphate (CaSO_4). The residue on the filter marked No. 3 is dried, then transferred to a platinum crucible and fused with anhydrous carbonate of soda; cool, and then place crucible and contents in a small beaker; add a little water, and heat to nearly 100°C . Filter and wash well the residue. The filtrate contains the silica and alumina combined with the alkali, while the residue on the filter is carbonate of barium. Dissolve the barium precipitate in hydrochloric acid, dilute with a little water and add excess of sulphuric acid. The precipitate of sulphate of barium is washed, dried, ignited, and weighed as BaSO_4 . The residue on the filter is acidified with hydrochloric acid and evaporated to dryness on the water-bath, a few drops more of the acid added and a little hot water, and the whole contents of the basin washed on to a filter. The residue is gelatinous silica, which is washed, dried, ignited, and weighed as SiO_2 . In the filtrate, which is made alkaline with ammonia, and the precipitate boiled, filter, wash, dry, and ignite as Al_2O_3 . Calculate the amount found to clay $\text{Al}_2(\text{SiO}_3)_2$.

Linseed Oil.

The inferior qualities of a linseed oil may not only be derived from the quality of the seed expressed, but also from its admixture with mineral and other oils, which are purposely added for profit.

The following is a complete testing of linseed oil to determine its quality:—

(a) *Specific Gravity*.—The density should be .930 at 15° C.

(b) *Solidifying Point*.—From -20° to -27° C.

(c) *Colour Re-action with Strong Sulphuric Acid*.—On adding one drop of the acid to a few drops of the oil placed in a watch-glass, resting on a sheet of white paper, the colour changes to blackish-brown.

(d) *Mineral Oil*.—The mineral oil present is estimated by weighing into a beaker 10 grms. of the oil, and adding 50 c.c. of an alcoholic solution of potash (80 grms. KHO to 1 litre of 98 per cent. alcohol); heat on the water-bath for fifteen minutes, with frequent stirring, and then add 50 c.c. of water and allow to cool. On cooling, 30 c.c. of ether are mixed with the soap solution, and the contents of the beaker are transferred to a separating funnel. Shake well, and allow to stand for two hours. The two layers of liquid represent (1) the ether solution containing the mineral oil, and (2) the soap solution containing the fatty acids. The ether solution is run into a tared flask, which is placed in an air oven and heated to 105° C. for eight hours. On cooling, the flask is re-weighed, the difference in the two weighings representing the amount of mineral oil in the sample taken.

In the soap solution, the fatty acids forming the linseed and any other fat oil added are determined according to the method described on page 208.

(e) *Elaidin Test*.—This test depends on the production of a solid elaidin by the action of nitric acid on the olein of fatty oils other than linseed oil. With the latter a liquid product solely is formed. Poutet and Archbutt, make the test by dissolving 1 c.c. of mercury in 12 c.c. cold nitric acid, taking 2 c.c. of the solution and adding it to 50 c.c. of the oil to be tested, placed in a flask. The temperature is kept at 10° to 15° C., and the contents are agitated every ten minutes for two hours. The mixture should remain liquid with pure oil.

(f) *Drying Properties*.—To ascertain the drying qualities of the sample of oil, 5 grms. are weighed into a shallow porcelain dish, or preferably a watch-glass, to a temperature of 100° C., in a water oven, for four hours; the oil should then become thick and refuse to flow, with a tendency to "skin" on the surface. The increase of weight from absorption of oxygen will average .25 per cent. per hour in a pure oil.

(g) *Saponification Value*.—The saponification value of an oil is the number of grammes of oil decomposed by a normal solution of potash (KHO) or soda (NaHO), and it is found by dividing the percentage of potash or soda required for saponification into 5610 for the former and 4000 for the latter. With the presence of mineral oil the saponification value of a so-called linseed oil is lowered in proportion to the amount present, owing to the non-saponifiable nature of the added oil. From this difference in saponification value the percentage amount of the adulterant may be calculated. The values for good raw and boiled oil are 193 and 190 respectively.

Oil of Turpentine.

Commercial oil of turpentine is very often adulterated with light tar oils, petroleum spirit, and resin spirit. For

their detection the refractometer is used. This instrument, invented by Jean and Amagat (see full instructions for use in Dr. Muter's article in *Analyst*, May 1890), is first set with good oil of turpentine, and then the genuine is run out of the prism and the sample is substituted. The presence of either light oil of tar or of petroleum spirit is shown by the powerful left-handed refraction produced. Thus 10 per cent. of light oil of tar present in the sample will produce a deviation of 40° , while the same amount of petroleum spirit will deviate about 15° .

Pure American turpentine has a specific rotatory power of $+21.5^\circ$.

Colour Tests of Ground White Lead.

To compare the shade of a sample with a standard ground lead, take a portion from each with a palette knife, and press together on a glass plate until the samples unite. The line of contact will be clearly marked if they are not identically of the same shade.

Dry White Lead.

Dry white lead is often found adulterated with the sulphates and carbonate of barium, sulphate and carbonate of lime, clay, sulphate of lead, etc.

These adulterants act mainly in lowering the density and opacity of the lead, and consequently in proportion to the amount present the white lead loses in covering power when applied with the brush.

They are estimated by dissolving the sample in acetic acid and bringing the whole to the boil, then filtering and washing, and proceeding as in the residue No. 2 and filtrate No. 2 in the analysis of white lead paint (p. 208).

Red Lead.

Red oxide of iron and brick-dust are sometimes used to adulterate red lead. They are detected by the simple method given on page 121, or by dissolving the red lead in hot dilute nitric acid, when the brick-dust remains insoluble. The oxide of iron is found by boiling red lead in dilute hydrochloric acid, filtering, and adding a solution of ferrocyanide of potassium; a dark precipitate of Prussian blue indicates iron.

TABLES.

TABLE OF ATOMIC WEIGHTS.

Element.	Symbol.	Atomic Weight.	Element.	Symbol.	Atomic Weight.
Aluminium . . .	Al.	27	Nickel . . .	Ni.	58.7
Antimony . . .	Sb.	119.9	Niobium . . .	Nb.	93.9
Arsenic . . .	As.	75	Nitrogen . . .	N.	14
Barium . . .	Ba.	137	Osmium . . .	Os.	195
Bismuth . . .	Bi.	208	Oxygen . . .	O.	16
Boron . . .	B.	10.9	Palladium . . .	Pd.	106
Cadmium . . .	Cd.	112	Phosphorus . . .	P.	31
Cesium . . .	Cs.	133	Platinum . . .	Pt.	195.5
Calcium . . .	Ca.	40	Potassium . . .	K.	39.1
Carbon . . .	C.	12	Rhodium . . .	Rh.	104.3
Cerium . . .	Ce.	141.5	Rubidium . . .	Rb.	85.4
Chlorine . . .	Cl.	35.5	Ruthenium . . .	Ru.	103.8
Chromium . . .	Cr.	52	Scandium . . .	Sc.	44
Cobalt . . .	Co.	58.7	Selenium . . .	Se.	79
Copper . . .	Cu.	63	Silicon . . .	Si.	28
Dicynium . . .	Di.	145	Silver . . .	Ag.	108
Erbium . . .	Er.	168.4	Sodium . . .	Na.	23
Fluorine . . .	Fl.	19	Strontium . . .	Sr.	87.5
Gallium . . .	Ga.	70.1	Sulphur . . .	S.	32
Gadolinium . . .	Gd.	91	Tantalum . . .	Ta.	182.7
Gold . . .	Au.	197	Tellurium . . .	Te.	128
Hydrogen . . .	H.	1	Thallium . . .	Tl.	204
Iodine . . .	I.	127	Thorium . . .	Th.	232.5
Iridium . . .	Ir.	193	Tin . . .	Sn.	117
Iron . . .	Fe.	56	Titanium . . .	Ti.	48
Lanthanum . . .	La.	138.9	Tungsten . . .	W.	184
Lead . . .	Pb.	207	Uranium . . .	U.	240.5
Lithium . . .	Li.	7	Ytterbium . . .	Yb.	173
Magnesium . . .	Mg.	24	Yttrium . . .	Y.	89.8
Manganese . . .	Mn.	55	Zinc . . .	Zn.	65
Mercury . . .	Hg.	200	Zirconium . . .	Zr.	90.6
Molybdenum . . .	Mo.	96.2			

TABLE OF THE COMBINATION OF COLOURS TO PRODUCE A
REQUIRED TINT.

he first-named colour is the principal ingredient, and the others follow in the order of their importance. Thus, in mixing a limestone tint, white is the principal ingredient, and red the colour least needed. The exact proportion of each depends on the shade required (DICK).

Compound Colours.	Simple Colours Needed.
Buff	White ; yellow ochre ; red.
Chestnut	Red ; black ; yellow.
Chocolate	Raw umber ; red ; black.
Claret	Red ; umber ; black.
Copper	Red ; yellow ; black.
Dove	White ; vermilion ; blue ; yellow.
Drab	White ; yellow ochre ; red ; black.
Fawn	White ; yellow ; red.
Flesh	White ; yellow ochre ; vermilion.
Freestone	Red ; black ; yellow ochre ; white.
French grey	White ; Prussian blue ; lake.
Gold	White ; stone ochre ; red.
Green bronze	Chrome green ; black ; yellow.
Green pea	White ; chrome green.
Grey	White lead ; black.
Lemon	White ; chrome yellow.
Limestone	White ; yellow ochre ; black ; red.
Olive	Yellow ; blue ; black ; white.
Orange	Yellow ; red.
Peach	White ; black ; blue.
Pink	White ; vermilion ; lake.
Purple	Violet, with more red and white.
Rose	White ; madder lake.
Sandstone	White ; yellow ochre ; black ; red.
Snuff	Yellow ; Vandyke brown.
Violet	Red ; blue ; white.

TABLE SHOWING THE PERCENTAGE AMOUNTS BY WEIGHT OF
DIFFERENT PIGMENTS REQUIRED TO PRODUCE VARIOUS
TINTS WITH ZINC WHITE (PAYEN).

Tint.	Composition.
Azure blue	1 part indigo.
Pearl blue	1 „ charcoal.
Slate blue	100 parts zinc dust.
Straw yellow	2½ „ lead chromate.
Chamois	{ 3 „ yellow ochre.
	{ 3 „ cinnabar.
Lemon yellow	{ 2½ „ chrome yellow.
	{ 2½ „ Prussian blue.
Gold colour	10 „ chrome yellow.
Water green	8 „ Prussian blue.

Tint.	Composition.
Grass green	{ 100 parts chrome yellow.
	8 „ Prussian blue.
Olive green	{ 50 „ yellow ochre.
	12 „ ivory black.
	50 „ yellow ochre.
Bronze green	{ 12 „ chrome yellow.
	6 „ Prussian blue.
	6 „ ivory black.

TABLE OF THERMOMETRIC DEGREES.

Centigrade.	Fahrenheit.	Reaumur.
Freezing 0°	Freezing 32°	Freezing 0°
„ 5°	„ 41°	„ 4°
„ 10°	„ 50°	„ 8°
„ 15°	„ 59°	„ 12°
„ 20°	„ 68°	„ 16°
„ 25°	„ 77°	„ 20°
„ 30°	„ 86°	„ 24°
„ 35°	„ 95°	„ 28°
„ 40°	„ 104°	„ 32°
„ 45°	„ 113°	„ 36°
„ 50°	„ 122°	„ 40°
„ 55°	„ 131°	„ 44°
„ 60°	„ 140°	„ 48°
„ 65°	„ 149°	„ 52°
„ 70°	„ 158°	„ 56°
„ 75°	„ 167°	„ 60°
„ 80°	„ 176°	„ 64°
„ 85°	„ 185°	„ 68°
„ 90°	„ 194°	„ 72°
„ 95°	„ 203°	„ 76°
Boiling 100°	Boiling 212°	Boiling 80°

Rules for Conversion.

Fahrenheit to Centigrade	$\frac{5 (F - 32)}{9} = C.$
Fahrenheit to Reaumur	$\frac{4 (F - 32)}{9} = R.$
Centigrade to Fahrenheit	$\frac{C \times 9}{5} + 32 = F.$
Centigrade to Reaumur	$\frac{C \times 4}{5} = R.$
Reaumur to Fahrenheit	$\frac{R \times 9}{4} + 32 = F.$

ANALYSIS OF RAW AND FINISHED PRODUCTS 219

TABLE SHOWING THE HEAT AND ELECTRICAL CONDUCTING POWER OF WELL-KNOWN METALS.

Order of Heat Conducting Power.	Order of Electrical Conducting Power.
Gold.	Copper.
Platinum.	Gold.
Silver.	Silver.
Copper.	Zinc.
Iron.	Platinum.
Zinc.	Iron.
Tin.	Tin.
Lead.	Lead.

TABLE SHOWING PERCENTAGE COMPOSITION OF SOME CLASSES OF BUILDING STONES (DANIELL AND WHEATSTONE).

Nature of Stone.	Sandstones.		Magnesian Limestones.		Oolites.	
Name of Locality.	Darley Dale.	Heddon.	Park Nook.	Bolsover.	Bath Box.	Ketton.
Silica	96·40	95·10	...	3·60
Carbonate of lime	0·36	0·80	55·70	51·10	94·52	92·17
Carbonate of magnesia	41·60	40·20	2·50	4·10
Iron and alumina	1·30	2·30	0·40	1·80	1·20	0·90
Water and loss	1·94	1·80	2·30	3·30	1·78	2·83
Bitumen	traces	traces
	100·00	100·00	100·00	100·00	100·00	100·00

TABLE OF THE ALLOYS OF LEAD, TIN, AND BISMUTH, AND THEIR MELTING-POINTS.

Parts Lead.	Parts Tin.	Parts Bismuth.	Melting-Point Fahr.
25	1	0	558°
10	1	0	541°
5	1	0	511°
3	1	0	482°
2	1	0	441°
1	1	0	370°
1	1½	0	334°
1	2	0	340°
1	3	0	356°

TABLE OF THE ALLOYS OF LEAD, Etc.—*Continued.*

Parts Lead.	Parts Tin.	Parts Bismuth.	Melting-Point Fahr.
1	4	0	365°
1	5	0	378°
1	6	0	381°
4	4	1	320°
3	3	1	310°
2	2	1	292°
1	1	1	254°
2	1	2	236°
3	5	3	202°
5	3	8	197°

TABLE OF THERMAL EQUATIONS FOR THE METALLURGICAL OPERATIONS IN LEAD AND ZINC SMELTING (ROBERTS-AUSTEN).

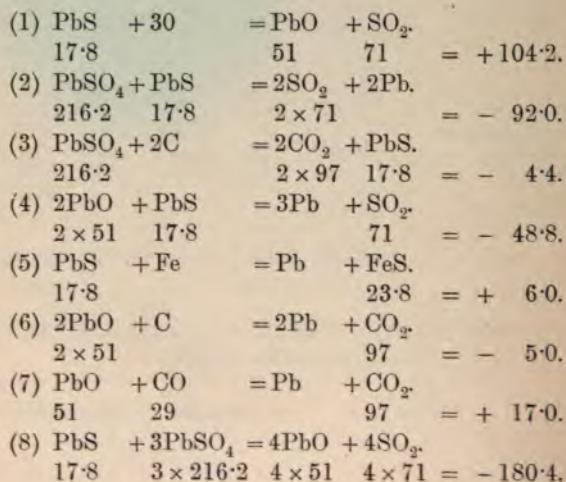
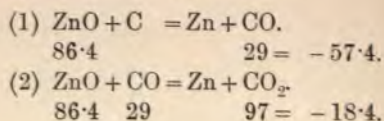
Lead.*Zinc.*

TABLE OF THE PHYSICAL PROPERTIES OF METALS.

Name of Metal.	Weight of a Cb. In. in Lbs.	Tenacity in Lbs. per Sq. In.	Crushing Force in Lbs. per Sq. In.
Antimony . .	·242	1,066	...
Bismuth . . .	·35	3,250	...
Brass (cast) . .	·30	17,978	10,300
Copper (cast) . .	·32	19,072	11,700
Gold	·70	20,400	...
Gun metal . . .	·30	36,000	...
Iron (wrought) .	·28	60,000	38,000
Lead (cast) . .	·41	1,824	7,000
Mercury	·49
Silver	·38	41,000	...
Steel	·28	12,000	...
Tin	·26	5,000	15,000
Zinc	·25	8,000	...

TABLE OF THE WEIGHTS OF VARIOUS MINERALS.

1 cb. ft. of water weighs $62\frac{1}{2}$ lb. at a temperature of 60° F. By ascertaining the spec. grav. of a substance and multiplying with $62\frac{1}{2}$, the exact weight of 1 cb. ft. in lbs. is obtained.

Mineral.	Lbs. (Avoird.) 1 Cb. Ft. Weighs.	Mineral.	Lbs. (Avoird.) 1 Cb. Ft. Weighs.
Anthracite coal . .	94	Calamine	190
Grey copper . . .	300	Fluor spar	186
Antimonial silver .	600	Flint	110
Arsenical iron pyrites .	370	Galena	465
Barytes	310	Limestone (hydraulic)	150
Witherite	248	,, (magnesian)	130
Building stone com- prising granite, gneiss, syenite, etc.	186	Iron pyrites . . .	280
		Tin ore	434
		Red zinc ore . . .	331

TABLE OF THE WEIGHTS OF 1 SQUARE FOOT OF LEAD AND COPPER IN LBS., FROM $\frac{1}{32}$ TO $\frac{1}{2}$ INCH IN THICKNESS.

Thickness.	Lbs. Lead.	Lbs. Copper.
$\frac{1}{32}$ inch	1·85	1·45
$\frac{1}{16}$ "	3·70	2·90
$\frac{3}{32}$ "	5·54	4·35
$\frac{1}{8}$ "	7·39	5·80
$\frac{5}{32}$ "	9·24	7·26
$\frac{3}{16}$ "	11·08	8·71
$\frac{7}{32}$ "	12·93	10·16
$\frac{1}{4}$ "	14·77	11·61
$\frac{9}{32}$ "	16·62	13·07
$\frac{5}{16}$ "	18·47	14·52
$\frac{11}{32}$ "	20·31	15·97
$\frac{3}{8}$ "	22·16	17·41
$\frac{13}{32}$ "	24·00	18·87
$\frac{7}{16}$ "	25·85	20·32
$\frac{15}{32}$ "	27·70	21·77
$\frac{1}{2}$ "	29·55	23·22

TABLE SHOWING IN THEIR ORDER THE COMPARATIVE PROPERTIES OF WELL-KNOWN METALS.

Order of Malleability.	Order of Ductility.	Order of Brittleness.	Order of Tenacity.	Order of Fusibility.
Gold	Gold	Antimony	Iron	Tin
Silver	Silver	Arsenic	Copper	Bismuth
Copper	Platinum	Bismuth	Platinum	Lead
Tin	Iron	Chromium	Silver	Zinc
Cadmium	Copper	Cobalt	Gold	Antimony
Platinum	Zinc	Manganese	Zinc	Silver
Lead	Tin	Molybdenum	Tin	Copper
Zinc	Lead	Tellurium	Lead	Gold
Iron	Nickel	Titanium	...	Iron
Nickel	Palladium	Tungsten	...	Nickel
Potassium	...	Uranium	...	Manganese

THE END.

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